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THE SPECIFIC HEATS OF CRYSTALS

Part I. General Theory

By Sir C. V. Raman

(*Memoir No. 87 of the Raman Research Institute, Bangalore 6*)
Received October 12, 1956

1. Introduction

The quantum theory of the specific heats of crystals proposed by Einstein in the year 1907 regards a crystal as an assembly of an immense number of harmonic oscillators with specific frequencies, the energy of vibration of which obeys the quantum rule; these oscillators form a system in thermodynamic equilibrium of which the behaviour can be described statistically with the aid of Boltzmann's theorem. Einstein identified these oscillators with the structural units (" Elementargebilde ") in the crystal and assumed that they could be grouped into sets, each set comprising a great number of oscillators characterised by a common frequency of vibration; the total number of oscillators of all sorts is taken to be thrice the number of atoms comprised in the crystal. He showed it to be a consequence of his theory that the thermal properties of a crystal would stand in the closest relationship with its spectroscopic behaviour.

The assumptions on which Einstein's theory rests are clearly justified by the physical facts of the case. For, every crystal consists of an immense number of structural units similar to each other which are capable of mechanical vibration and which by reason of their similarity may be expected to exhibit identical dynamical behaviour. The theory is, in effect, a synthesis of the results indicated by classical dynamics for such a system with the notions of the quantum theory and the basic principles of thermodynamics. It involves no inherent contradictions and can therefore claim to be a rational approach to the fundamental problems of crystal physics. The following questions, however, need to be answered before any use can be made of the theory. How are the oscillators of different sorts envisaged in the theory related to the known structure of a crystal ? How are they to be enumerated ? What is the procedure by which the characteristic frequency of each set of oscillators may be evaluated ? The present memoir concerns itself with finding the answers to these questions and thus giving form and substance to the ideas of a very general nature put forward by Einstein.

2. THE NORMAL VIBRATIONS OF CRYSTAL STRUCTURES

That the specific heat of a crystalline solid tends with rising temperature to reach a limiting value proportional to the number of atoms comprised in it is a clear indication that the theoretical approach to any explanation of the facts has of necessity to consider the subject from an atomistic standpoint. We have also to recognize the existence of interatomic forces; hence, the movements with which we are concerned are not simple translations of the individual atoms but vibrations of the atoms about their positions of equilibrium in the structure of the crystal. Any attempt to describe these vibrations or to enumerate them has necessarily to be based on the fundamental theorem in classical mechanics which states that all the possible small vibrations of a connected system of particles about their positions of equilibrium are summations of an enumerable set of normal modes; in each such normal mode, the particles of the system have all the same frequency and the same or opposite phases of vibration. Hence, any rational approach to the specific heat problem must of necessity start with a consideration of the normal modes of vibration—in the sense of the theorem just stated—of the atoms about their positions of equilibrium in the lattice structure of the crystal.

The basic principle of crystal architecture is that the structure comes into coincidence with itself following a unit translation along any one of the three axes of the lattice. It follows as a necessary consequence that the normal modes of vibration of the atoms characteristic of the structure of the crystal should possess the same property. This can evidently happen in two ways, thereby enabling us to divide the normal modes into two distinct classes. In the first class of normal modes, the amplitudes as well as the phases of oscillation of the equivalent atoms which come into coincidence following a unit translation are identical. In the second class of normal modes, the amplitudes of equivalent atoms are the same but the phases are all reversed and the normal mode therefore remains the same following the unit translation. Since these two alternatives are possible for a unit translation along each of the three axes of the lattice, we have $2 \times 2 \times 2$ or 8 possible situations. Considering each of these situations separately, we proceed to write down the equations of motion of the p atoms comprised in the unit cell in terms of the $3p$ co-ordinates which determine their displacements. Since the displacements of the equivalent atoms in adjoining cells which interact with the atoms in the cell under consideration are also the same, the $3p$ equations of motion of the latter contain only $3p$ independent co-ordinates. They can therefore be completely solved, giving us $3p$ solutions for each of the eight possible situations referred to above. Thus in all, we have $24p$ solutions. $(3p-3)$

of these solutions represent normal modes of vibration of the first kind, $21\,p$ solutions represent normal modes of the second kind and the three remaining solutions represent simple translations which have necessarily to be excluded.

The $(24\,p - 3)$ normal modes of vibration of the atoms in a crystal indicated by the theory may be regarded as the modes of *internal* vibration of the group of $8\,p$ atoms comprised in a super-cell of the crystal lattice whose linear dimensions are twice as large as that of the unit cell consisting of p atoms. The three omitted solutions would then represent the translations along each of the three axes of the crystal lattice of the whole group of $8\,p$ atoms included in the super-cell. Thus, we recognise that the structural unit whose dynamical behaviour is representative of the entire crystal is not the unit cell of the crystal structure, but has twice its dimensions along each of the three axes of the lattice.

Thus, following Einstein, we may regard a crystal as an assembly of $(24\,p - 3)$ sets of oscillators, each of the sets having its own distinctive frequency of vibration. The number of oscillators in each set is the same as the number of super-cells containing $8\,p$ atoms which are included in the whole crystal. Each set of oscillators forms an assembly in thermodynamic equilibrium and its behaviour can therefore be described statistically with the aid of Boltzmann's theorem. The average energy of an oscillator in each set is given by Einstein's formula for the particular frequency. Multiplying this by the number of super-cells contained in the volume of the crystal, we obtain an expression for the energy of all the oscillators in that set. Finally, summing up the expressions thus obtained for all the $(24\,p - 3)$ sets with their respective frequencies of vibration, we obtain an expression for the thermal energy arising from the excitation of the vibrations of the atoms having precisely specifiable frequencies.

3. The Vibration Spectra of Crystals

The foregoing results may be summed up as follows. If a unit volume of the crystal contains S super-cells each including $8\,p$ atoms, the total number of degrees of atomic freedom is $24\,p$S; a very large proportion of this number, *viz.*, $(24\,p - 3)$ S degrees of freedom, appears in the vibration spectrum of the crystal as sharply defined monochromatic frequencies; $(3\,p - 3)$ of these frequencies represent vibrations in which equivalent atoms contained in each super-cell have the same amplitudes and phases of vibration, while the $21\,p$ other frequencies represent modes of vibration in which the amplitudes are the same but the phases are opposite for equivalent atoms along one, two or all three of the axes of the lattice.

We have now to consider and determine the nature of the movements represented by the 3 S degrees of atomic freedom left out in the preceding enumeration. This is also the number of degrees of freedom of translation of the S super-cells included in the crystal. Any translation of an individual super-cell would necessarily set up forces resisting such movement and also tending to displace neighbouring super-cells. We are therefore led to assume that the 3 S degrees of freedom under discussion would manifest themselves as internal modes of vibration in elements of volume of larger dimensions than our super-cell. The larger such element of volume is, the lower would be the limit of the possible frequencies of such vibration. The translations of the individual super-cells are therefore to be associated with a whole series of frequencies lying between zero and an upper limit which is set by the frequency of internal vibrations in our super-cell. To take account of the anisotropy of the crystal, we would, in general, have to assume separate upper limits of frequency for the translations along the three axes of the crystal. It is left to determine how the 3 S unassigned degrees of freedom are distributed amongst the oscillators of various frequencies lying in the permitted ranges $0 \rightarrow \nu_x$, $0 \rightarrow \nu_y$, $0 \rightarrow \nu_z$.

The problem indicated above can be dealt with and solved in a very simple manner. Consider two volume elements in the crystal which have the same shape as our super-cell and whose dimensions are respectively m and n times larger. The number of degrees of freedom of translation of these enlarged super-cells is respectively three times the number of such cells included in the volume of the crystal; the difference between them, *viz.*, $3\,S\,(1/m^3 - 1/n^3)$ would therefore be the number of oscillators whose frequencies lie between ν_m and ν_n which are respectively their lowest frequencies of internal vibration. But the principle of dynamical similarity enables us to write $\nu_m = k/m$ and $\nu_n = k/n$ where k is a constant having the dimensions of a frequency. Hence, as m approaches n, $\nu_m - \nu_n$ may be set equal to $d\nu$ and the number of oscillators whose frequencies lie between ν_m and ν_n may be written as $9\,S\,\nu^2\,d\nu/k^3$. On integrating this between zero and ν_l (the upper limit of the permitted frequencies), we should recover 3 S as the total number of oscillators, and hence k^3 is identified as ν_l^3. Accordingly, the law of distribution of frequency in the spectrum may be written as $9\,S.\,\nu^2 d\nu/\nu_l^3$ for the isotropic case. More generally, for an anisotropic crystal ν_l may be replaced by ν_x or ν_y or ν_z respectively for the three directions of translations and the numerical factor 9 is replaced by 3.

The law of distribution of the frequencies thus derived indicates that the majority of the oscillators now under consideration have frequencies not far removed from the upper limit. The same result may be expressed other-

wise by the statement that the majority of the oscillators are of very small dimensions not far removed from the lower limit, namely the dimensions of the super-cell. If, for example, we were to identify *all* the vibrations arising from the translations of the super-cell with the internal vibrations in a volume element whose dimensions are *twice* those of the super-cell, we would not be seriously in error. All except one-eighth of the 3 S degrees of freedom would be accounted for in such an enumeration; the residue omitted would represent oscillations in still larger volume elements appearing with still lower frequencies.

4. The Thermal Energy of Crystals

The atomistic approach to the specific heat problem proposed by Einstein, when fully developed, thus leads us to the following picture of the nature of the vibrations in a crystal which are the carriers of the thermal energy. The oscillating units are *not* the unit cells of the structure, but are twice as large as the unit cells in their linear dimensions; their oscillations are of two kinds, namely, those arising from their internal vibrations and those arising from their translatory movements. The oscillations of the former description appear with $(24\,p - 3)$ discrete frequencies of vibration, p being the number of atoms contained in the unit cells of the crystal structure. The translatory movements, on the other hand, appear with a spectrum of frequencies all of which are lower than those of the internal vibrations. These, for the most part, are concentrated near the upper limit of their permitted range; but there is a residue which tails off as a continuous spectrum to very low frequencies.

Accordingly, making use of the reasoning employed by Einstein for evaluating the average energy of an oscillator in each of the sets under consideration, we obtain the following expression for the heat content of a volume of a crystal containing N unit cells of the crystal structure as a function of the temperature, namely

$$\frac{N}{8}\left[\sum_{i=1}^{24p-3}\frac{h\nu_i}{e^{h\nu_i/kT}-1}+\frac{3}{\nu_l^3}\int_0^{\nu_l}\frac{3h\nu^3 d\nu}{e^{h\nu/kT}-1}\right]$$

The numerical factor 1/8 appears in the expression because each dynamic unit contains 8 unit cells of the crystal structure. On differentiating the expression with respect to T as usual, we get the formula for the specific heat.

The following remarks may be made regarding the numerical evaluation of the expression given above. All the $(24\,p - 3)$ frequencies would be distinct from each other only in the case of a completely anisotropic crystal.

If any symmetry elements are present, the number of distinct frequencies would be naturally diminished and the formula would then contain only such smaller number, but the individual terms would then have to be multiplied by their respective degeneracies. Such reduction in the number of distinct frequencies would naturally appear both in respect of the $(3p - 3)$ frequencies in which both the amplitudes and the phases are the same in adjacent unit cells and in the $21p$ others in which the phases may be opposite as already explained. As an illustration of these remarks, we may consider a case in which $p = 2$ and the crystal belongs to the cubic class and its structure consists of two interpenetrating face-centred cubic lattices. The $(3p - 3)$ distinct frequencies then reduce to a single triply degenerate frequency; the $21p$ or 42 other vibrations reduce to only eight distinct frequencies, all of which may be readily described in geometric terms related to the structure of the crystal.

Since the first term in the expression for the thermal energy is a summation extended over $(24p - 3)$ distinct modes of vibration, while the second represents only the three residual translations, it is evident that the latter would be of very minor importance relatively to the first, especially in those cases where p is very large, in other words when the crystal has a multi-atomic structure. The position is a little different when p is small, as for example, when p is equal to 1. The contribution from the second term would not then be altogether negligible in comparison with the first term. The second term also acquires some importance relatively to the first at very low temperatures. For, since the frequencies appearing in it are low, their contributions to the specific heat would survive when those due to the vibrations of the higher frequencies appearing in the first term have been effectively frozen out by reason of Boltzmann's theorem.

5. THE SPECTROSCOPIC BEHAVIOUR OF CRYSTALS

In his paper of 1907, Einstein emphasised the intimate relationship indicated by his theory between the thermal properties of crystal and their optical behaviour. It is appropriate therefore that we make a reference here to the decisive support given to the results of the theory set forth above by the experimental facts regarding the spectroscopic behaviour of crystals revealed by investigations made with a great variety of materials and by diverse techniques of investigation. We need not however dilate on this topic, since the experimental situation in this respect has been reviewed in my Lindau address, and since, moreover, the particular case of the diamond which illustrates the general principles in a very striking fashion has been dealt with in detail in a recent lecture published in these *Proceedings*.

6. Summary

In Einstein's atomistic approach to the specific heat problem, a crystal is regarded as an assembly of sets of individual harmonic oscillators, each set consisting of a great number of oscillators having a common frequency of vibration. In the present paper, this view is developed and an expression is obtained for the thermal energy of the crystal which appears as a summation of $(24\,p - 3)$ terms arising from the individual monochromatic frequencies of internal vibration of the dynamic units of the crystal structure each containing $8\,p$ atoms, with a supplementary term which takes account of the translational movements of the same units manifesting themselves as a continuous spectrum of frequencies of vibration within the crystal.

THE SPECIFIC HEATS OF CRYSTALS

Part II. The Case of Diamond

By Sir C. V. Raman

(*Memoir No.* 87 *of the Raman Research Institute, Bangalore* 6)

Received October 15, 1956

In a lecture on the diamond published in the September issue of these *Proceedings* (Vol. 44, 1956, p. 99), the vibrations of the diamond structure were discussed in detail and the results of spectroscopic investigations on the nature of the vibration spectrum were also set forth. The results contained in that paper furnish us with all the material necessary for a complete theoretical evaluation of the specific heat of diamond over the entire range of temperatures for which experimental data are available. We shall now proceed to make such an evaluation and compare it with the results of the published measurements on the specific heat of diamond.

Table I gives a list of the nine characteristic frequencies of the diamond structure expressed in wave-numbers ($cm.^{-1}$), their respective degeneracies and the geometric description of the corresponding modes of vibration. The frequencies shown in the last column of the table were evaluated with the aid of the equations of motion and a set of force constants and were also independently confirmed by the results of spectroscopic investigation by several

Table I

Vibration Spectrum of Diamond

No.	Degeneracy	Description of the mode	Frequency in $cm.^{-1}$
I ..	3	Oscillation of the two interpenetrating lattices against each other	1332
II ..	8	Tangential oscillation of the octahedral planes	1250
III ..	6	Tangential oscillation of the cubic planes	1239
IV ..	4	Normal oscillation of the octahedral planes	1149
V & VI ..	(3+3)	Normal oscillation of the cubic planes	1088
VII ..	4	Normal oscillation of the octahedral planes	1008
VIII ..	6	Tangential oscillation of the cubic planes	740
IX ..	8	Tangential oscillation of the octahedral planes	621

different techniques. It is a simple matter with the aid of the table to calculate the contributions to the specific heat arising from the nine modes of internal vibration of the diamond structure. The lowest frequency appearing in the table expressed in wave-numbers, *viz.*, 621 cm.$^{-1}$ may also be properly assumed to be the upper limit of frequency in the continuous spectrum of the vibrations arising from the translations of the super-cell of the crystal structure, as explained in Part I of the present paper.

The contribution to the specific heat arising from the continuous part of the vibration spectrum can be readily evaluated on this basis with the aid of the tabulated values of the relevant functions available in "Landolt-Bornstein". Table II below shows the results of such computations. The contributions to the atomic heat arising respectively from the discrete spectrum and from the continuous spectrum are shown separately for a series of temperatures ranging from 15° to 1100° on the absolute scale. The sum of the two contributions is also tabulated.

TABLE II

Theoretical Computation of the Atomic Heat of Diamond

(Calories per gram-atom per degree)

Absolute Temperature T°	Discrete Frequencies	Continuous Spectrum	Total	Absolute Temperature T°	Discrete Frequencies	Continuous Spectrum	Total
15	..	0·00014	0·00014	200	0·4069	0·1631	0·5700
20	..	0·00033	0·00033	225	0·5894	0·1895	0·7789
25	..	0·00064	0·00064	250	0·7844	0·2124	0·9968
30	..	0·0011	0·0011	275	1·0137	0·2319	1·2456
40	..	0·0026	0·0026	300	1·2418	0·2486	1·4904
50	..	0·0051	0·0051	350	1·700	0·275	1·975
60	..	0·0088	0·0088	400	2·139	0·294	2·433
70	0·0005	0·0140	0·0145	450	2·538	0·308	2·846
80	0·002	0·0207	0·0227	500	2·892	0·319	3·211
90	0·0056	0·0290	0·0346	600	3·469	0·334	3·803
100	0·0128	0·0388	0·0516	700	3·899	0·344	4·243
120	0·0419	0·0619	0·1038	800	4·224	0·350	4·574
140	0·0957	0·0877	0·1834	900	4·465	0·355	4·820
160	0·1758	0·114	0·2898	1000	4·653	0·358	5·011
175	0·2517	0·1333	0·3850	1100	4·797	0·360	5·157

The values of the atomic heats of diamond listed in Table II are exhibited in graphical form in Fig. 1. At temperatures below 70° absolute, the curve appears to touch the axis since the very low values of the specific heats in this region cannot be represented on the scale of the graph. The values in this region are, however, of great interest, since, as will be seen from

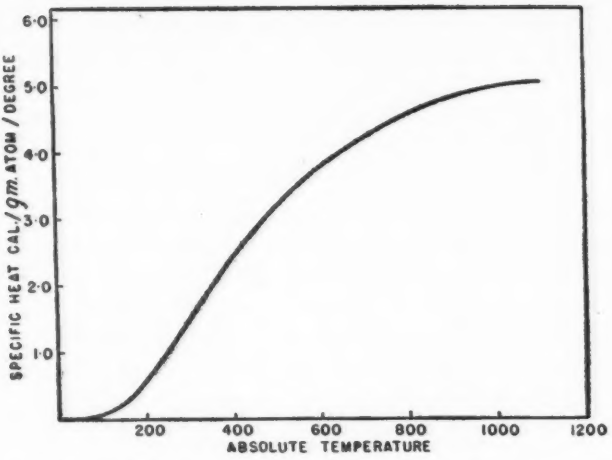

FIG. 1. The atomic heats of diamond calculated from the spectroscopic data.

Table II, they arise exclusively from the contribution of the continuous spectrum of frequencies which represents only 3 out of the 48 degrees of atomic freedom of movement of the crystal. Accordingly, the theoretical curve for this part of the temperature range has been drawn with a greatly enlarged scale for the ordinates in Fig. 2 below. Fortunately also, the specific heat of diamond in this region of temperature has been the subject of detailed investigation by Warren DeSorbo (*Journal of Chemical Physics*, Vol. 21, 1953, p. 876) and his experimental results for this very interesting region are plotted in the diagram. A gratifying agreement between theory and observation will be noticed.

The specific heat of diamond in the range of absolute temperatures from 70° to 300° was determined by K. S. Pitzer (*Journal of Chemical Physics*, Vol. 6, 1938, p. 68). The measurements by DeSorbo also cover this range. A careful inter-comparison between them shows that Pitzer's values are distinctly higher than those of DeSorbo throughout this range and that they also exhibit a scatter which is distinctly larger than the results of DeSorbo. DeSorbo's work is of later date and his data form a continuous sequence over a wider range of temperatures. For these reasons, it was felt that a comparison between theory and experiment would be more appropriately made with the results of DeSorbo. Fig. 3 below shows such comparison and here again a very satisfactory agreement emerges.

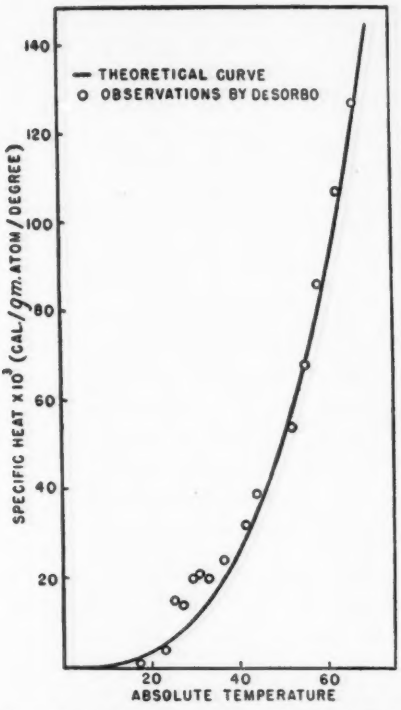

FIG. 2. Comparison between theory and experiment at very low temperatures.

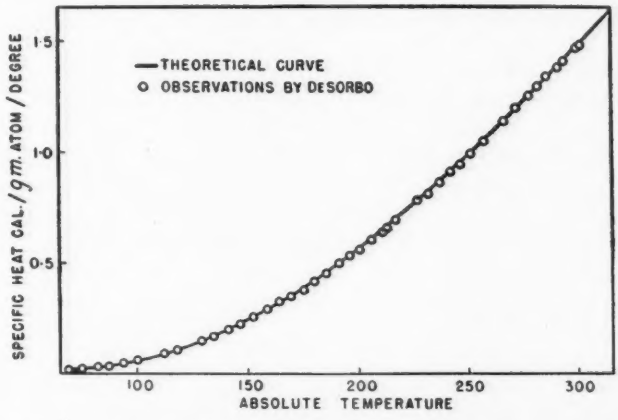

FIG. 3. Comparison of theory and experiment below room temperature.

Finally, Fig. 4 exhibits a comparison between the theoretical values and the experimental data in the temperature range from 300° to 1100° absolute covered by the determinations of Magnus and Hodler (*Annalen Der Physik*, Vol. 80, 1926, p. 808). The observed discrepancies throughout the range do not exceed two per cent. and in most cases are much less. The agreement should therefore be considered as satisfactory.

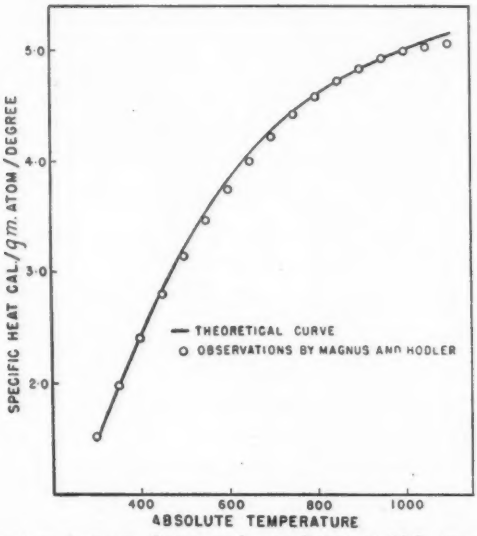

FIG. 4. Comparison between theory and experiment at high temperatures.

SUMMARY

The specific heat of diamond in the temperature range between 15° and 1100° absolute has been computed theoretically, making use of the nine spectroscopically determined vibration frequencies of the diamond structure as well as their known degeneracies, and further taking the lowest of these nine frequencies to be the upper limit of frequency in the residual continuous spectrum as explained in Part I of the paper. The results are compared with the experimental observations of DeSorbo from 15° to 300° absolute and of Magnus and Hodler from 300° to 1100° absolute. A highly satisfactory agreement between theory and experiment emerges.

ON THE DIFFRACTION OF LIGHT BY PROGRESSIVE SUPERSONIC WAVES

Oblique Incidence: Intensities in the Neighbourhood of the Bragg Angle

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(Communicated by Sir C. V. Raman, F.R.S., N.L.)

1. Introduction

In the case of oblique incidence, Bhatia and Noble[1] have shown that, if the angle of incidence ψ is close to the Bragg angle for the order -1, the expressions for the intensities differ from those in the case that the angle of incidence is very different from the Bragg angle. These authors give formulæ for the intensities of the orders 0 and -1. For the intensities of the orders $+1$ and -2, however, they only give expressions in the case of exact Bragg incidence.

The purpose of the present paper is to deduce these results from the generalised theory of Raman and Nath[2] and to give also expressions for the intensities of the orders $+1$ and -2 in the case that the angle of incidence is close to the Bragg angle.

2. The Results of Aggarwal[3]

According to the generalised theory of Raman and Nath, the amplitudes of the diffracted light waves satisfy the following system of difference—differential equations,

$$2\frac{d\phi_n}{d\xi} - (\phi_{n-1} - \phi_{n+1}) = i\,(n^2\rho - 2an\sin\psi)\,\phi_n \qquad (n = -\infty, \ldots, +\infty) \quad (1)$$

with the boundary conditions

$$\phi_0(0) = 1, \qquad \phi_n(0) = 0 \qquad (n \neq 0) \quad (2)$$

where

$$\xi = \frac{2\pi\mu_1 Z}{\lambda}$$

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§ At present at Rijksuniversiteit te Gent, Laboratorium voor Kristalkunde, Ghent, Belgium.

$$\rho = \frac{\lambda^2}{\mu_1 \mu_0 \lambda^{*2}} \,*$$

$$a = \frac{\lambda}{\mu_1 \lambda^*}$$

λ = the wave-length of the incident light in vacuum,

λ^* = the wave-length of the supersonic waves in the considered medium,

μ_0 = the refractive index of the undisturbed medium,

μ_1 = the maximum variation of the refractive index,

Z = the distance travelled by the light beam through the ultrasonic field,

ψ = the angle of incidence of the light.

Supposing $\phi_{\pm 2} = \phi_{\pm 3} = \cdots = 0$, Aggarwal has shown that if it is assumed, that the intensity $I_0 = 1$ and remains so when the lines of order $+1$ and -1 appear, the expressions for the first order intensities are given by

$$I_{\pm 1} = \left(\frac{\pi \mu_1 L}{\lambda}\right)^2 \frac{\sin^2\left[\frac{\pi L}{2\lambda^*}\left(\frac{\lambda}{\mu_0 \lambda^*} \pm 2 \sin \psi\right)\right]}{\left[\frac{\pi L}{2\lambda^*}\left(\frac{\lambda}{\mu_0 \lambda^*} \pm 2 \sin \psi\right)\right]^2} \tag{3}$$

L being the width of the sound field.†

We notice that the expressions (3) remain finite when the angle of incidence is equal to the Bragg angle ψ for the order -1, defined by

$$\sin \psi = \tfrac{1}{2} \cdot \frac{\lambda}{\mu_0 \lambda^*} = \frac{\rho}{2a}$$

One gets

$$I_{+1} = I_{-1} \frac{\sin^2\left(\frac{\pi \lambda L}{\mu_0 \lambda^{*2}}\right)}{\left(\frac{\pi \lambda L}{\mu_0 \lambda^{*2}}\right)^2} .$$

Now the intensity of order $+1$ may be neglected if $\frac{\lambda L}{\mu_0 \lambda^{*2}} \gtrapprox 1$. So it is

* The expression for ρ in the Raman-Nath theory contains a factor $\cos^2\psi$. Resuming the reasoning of those authors to obtain the system of difference—differential equations, but expressing the periodicity along the direction of propagation of the sound waves instead of along a direction normal to the incident light beam, one obtains the above value of ρ.

† In fact we should have to read $L/\cos\psi$ instead of L in Formula (3). In practice, however, the angle ψ is always very small, so that the distance traversed by the light in the ultrasonic field may be approximated by L.

evident that while for low frequencies of the ultrasonic waves the orders $+1$ and -1 appear simultaneously, for higher frequencies only the order -1 appears. I_0 remaining equal to unity and I_{-1} becoming maximum for Bragg incidence, *i.e.*, $I_{-1} = \left(\frac{\pi\mu_1 L}{\lambda}\right)^2$ is not very small, it is clear that when the angle of incidence is close to the Bragg angle, the expressions (3) are not more valid.

3. Intensities of the Orders 0 and -1

From the preceding section it is evident that we should obtain better expressions for the intensities of the orders 0 and -1, in the case of an angle of incidence close to the Bragg angle, if we assume that in the system (1) all the amplitudes, except ϕ_0 and ϕ_1, disappear. The system now becomes

$$\begin{cases} 2\dfrac{d\phi_0}{d\xi} + \phi_1 = 0 \\ 2\dfrac{d\phi_1}{d\xi} - \phi_0 = 4i\sigma\phi_1 \end{cases} \tag{4}$$

where

$$4\sigma = \rho - 2a\sin\psi \tag{5}$$

the boundary conditions still are

$$\phi_0(0) = 1,\ \phi_1(0) = 0 \tag{6}$$

The equations (4) form an easy system of differential equations of the second order, the solution of which, satisfying the boundary conditions (6) is,

$$\phi_0 = \left[\cos\sqrt{\sigma^2+\tfrac{1}{4}}\cdot\xi - \frac{i\sigma}{\sqrt{\sigma^2+\tfrac{1}{4}}}\sin\sqrt{\sigma^2+\tfrac{1}{4}}\cdot\xi\right]e^{i\sigma\xi} \tag{7}$$

$$\phi_1 = -\tfrac{1}{2}\cdot\frac{\sin\sqrt{\sigma^2+\tfrac{1}{4}}\cdot\xi}{\sqrt{\sigma^2+\tfrac{1}{4}}}\cdot e^{i\sigma\xi} \tag{8}$$

The intensities of the orders 0 and -1 immediately follow from (7) and (8). After effectuating the calculations we get,‡

$$I_0 = \phi_0\phi_0^* = \frac{1}{\sigma^2+\tfrac{1}{4}}\left[\sigma^2 + \tfrac{1}{4}\cos^2\sqrt{\sigma^2+\tfrac{1}{4}}\cdot\xi\right] \tag{9}$$

$$I_{-1} = \phi_1\phi_1^* = \tfrac{1}{4}\cdot\frac{\sin^2\sqrt{\sigma^2+\tfrac{1}{4}}\cdot\xi}{\sigma^2+\tfrac{1}{4}} \tag{10}$$

‡ Generally one has for the intensity of the order n, $I_n = \phi_{-n}\,\phi_{-n}^*$ in accordance with the preliminary theory of Raman and Nath, where I_n is found as the square of a Bessel function of the order $-n$.

4. INTENSITY OF THE ORDER -2

In order to compute this intensity, we shall follow Aggarwal's method: we assume that the expressions for the intensities of the orders 0 and -1 do not change when the line of order -2 appears. The amplitude of the order -2 can then be determined by the following differential equation of the system (1),

$$2\frac{d\phi_2}{d\xi} - \phi_1 = i(4\rho - 4a\sin\psi)\,\phi_2 \tag{11}$$

The solution of this differential equation satisfying the boundary conditions is

$$\phi_2 = -\tfrac{1}{4}\left[\frac{e^{ik_1\xi}}{(k_2-k_1)(k_1-k_3)} + \frac{e^{ik_2\xi}}{(k_1-k_2)(k_3-k_2)} + \frac{e^{ik_3\xi}}{(k_2-k_1)(k_3-k_1)}\right] \tag{12}$$

where

$$\begin{aligned} k_1 &= \sigma + \sqrt{\sigma^2+\tfrac{1}{4}} \\ k_2 &= \sigma - \sqrt{\sigma^2+\tfrac{1}{4}} \\ k_3 &= 2(\rho - a\sin\psi) \end{aligned} \tag{13}$$

The intensity of the order -2 consequently is given by

$$I_{-2} = \phi_2\phi_2^* = \tfrac{1}{4}[(k_2-k_3)(k_1-k_3)(k_1-k_2)]^{-1} \cdot \left\{\frac{\sin^2(k_3-k_2)\frac{\xi}{2}}{k_2-k_3} + \frac{\sin^2(k_3-k_1)\frac{\xi}{2}}{k_3-k_1} + \frac{\sin^2(k_1-k_2)\frac{\xi}{2}}{k_1-k_2}\right\} \tag{14}$$

Now if we only consider an exact Bragg incidence, so that

$$\sigma = 0,\ k_1 = \tfrac{1}{2},\ k_2 = -\tfrac{1}{2},\ k_3 = \rho,$$

the formula (14) becomes

$$I_{-2} = \tfrac{1}{4}\cdot\frac{1}{\rho^2-\frac{1}{4}}\left\{-\frac{\sin^2(\rho+\frac{1}{2})\frac{\xi}{2}}{\rho+\frac{1}{2}} + \frac{\sin^2(\rho-\frac{1}{2})\frac{\xi}{2}}{\rho-\frac{1}{2}} + \sin^2\frac{\xi}{2}\right\} \tag{15}$$

It is well known[4] that if only a few order lines appear in the diffraction spectrum, $\rho \gg 1$; so $\frac{1}{2}$ may be neglected with respect to ρ and the formula (15) finally becomes

$$I_{-2} = \tfrac{1}{4} \cdot \frac{1}{\rho^2} \sin^2 \frac{\xi}{2} \tag{16}$$

5. Intensity of the Order + 1

In the same way as in Section 4, we see that the amplitude of the order + 1 is determined by the differential equation

$$2 \frac{d\phi_{-1}}{d\xi} + \phi_0 = i(\rho + 2a \sin \psi)\phi_{-1} \tag{17}$$

Its solution satisfying the boundary conditions is

$$\phi_{-1} = -\frac{i}{2} \left[\frac{(k_1+k_2-k_4)\, e^{ik_4\xi}}{(k_1-k_4)(k_2-k_4)} + \frac{k_2\, e^{ik_1\xi}}{(k_2-k_1)(k_4-k_1)} + \frac{k_1\, e^{ik_2\xi}}{(k_1-k_2)(k_4-k_2)} \right] \tag{18}$$

where k_1 and k_2 have the same values as given by (13) and

$$k_4 = \tfrac{1}{2}(\rho + 2a \sin \psi) \tag{19}$$

Consequently the intensity of the order + 1 is

$$I_{+1} = \phi_{-1}\phi_{-1}^* = \tfrac{1}{4}[(k_1 - k_2)(k_1 - k_4)(k_4 - k_2)]^{-1} \cdot \left\{ \frac{4k_1k_2 \sin^2 (k_2-k_1)\frac{\xi}{2}}{k_2 - k_1} + \frac{4k_2(k_1+k_2-k_4)\sin^2(k_1-k_4)\frac{\xi}{2}}{k_1 - k_4} + \frac{4k_1(k_1+k_2-k_4)\sin^2(k_4-k_2)\frac{\xi}{2}}{k_4 - k_2} \right\} \tag{20}$$

If again we consider an exact Bragg incidence, so that

$$\sigma = 0, \quad k_1 = \tfrac{1}{2}, \quad k_2 = -\tfrac{1}{2}, \quad k_4 = \rho$$

this rather complicated expression becomes

$$I_{+1} = \tfrac{1}{4} \cdot \frac{1}{\rho^2 - \frac{1}{4}} \left\{ -\sin^2 \frac{\xi}{2} + \frac{2\rho}{\rho - \frac{1}{2}} \sin^2 (\rho - \tfrac{1}{2}) \frac{\xi}{2} + \frac{2\rho}{\rho + \frac{1}{2}} \sin^2 (\rho + \tfrac{1}{2}) \frac{\xi}{2} \right\} \tag{21}$$

Taking into account that $\rho \gg 1$, this formula reduces itself to

$$I_{+1} = \tfrac{1}{4} \cdot \frac{1}{\rho^2} \left[-\sin^2 \frac{\xi}{2} + 2 \sum_{+,-} \sin^2 (\rho \pm \tfrac{1}{2}) \frac{\xi}{2} \right] \tag{22}$$

or

$$I_{+1} = \tfrac{1}{4} \cdot \frac{1}{\rho^2} \left[- \sin^2 \frac{\xi}{2} + 4 \sin^2 \frac{\rho\xi}{2} \right] \tag{23}$$

where the symbol $\sum_{+,-}$ has the following meaning, $\sum_{+,-} f(a \pm b) = f(a + b) + f(a - b)$.

6. Comparison with the Results of Bhatia and Noble

There exists a simple relation between the maximum variation of the refractive index μ_1 and the maximum variation of the scattering index Δ used by Bhatia and Noble,

$$\Delta = \frac{2\mu_0\mu_1}{a}, \quad \text{where } a = \tfrac{1}{3}(\mu_0^2 + 2)(\mu_0^2 - 1) \approx 1$$

Using this relation and introducing the notations of Bhatia and Noble,

$$\delta = \Delta \left(\frac{\lambda^*}{\lambda} \right)^2, \qquad \beta = \frac{\pi\lambda}{\mu_0\lambda^{*2}}, \qquad \xi = \frac{\mu_0\lambda^*}{\lambda} \sin\psi$$

(it has to be noticed that this ξ has another meaning than the same notation used above) in the expressions (9), (10), (16) and (22) we obtain exactly formulæ (4·12 *a*), (4·12 *b*), (4·12 *c*) and (4·12 *d*) of Part II of their paper. It must be noted that formula (4·12 *d*) of those authors contains two printing errors, which were kindly confirmed to us by Dr. A. B. Bhatia.

7. Summary

It has been shown that in the case of oblique incidence of the light when the angle of incidence is close to the Bragg angle and for high frequencies of the supersonic waves, the intensities of the orders 0 and -1 and of the orders $+1$ and -2 can easily be obtained from the generalised theory of Raman and Nath. The formulæ are the same as those obtained by a more involved perturbation calculation by Bhatia and Noble.

We are very thankful to Dr. R. Mertens for the many fruitful discussions we had with him on this subject.

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EXISTENCE AND CLASSIFICATION OF PRODUCTS OF SUMMABILITY MATRICES

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Introduction

1. In this paper I prove theorems relating to the products of matrices which define either convergence preserving or limit preserving transformations of a series or a sequence into either a series or a sequence. The properties of sequence-to-sequence, series-to-sequence and series-to-series transformation matrices have been studied earlier by several authors and a comprehensive account of them can be found in Dienes[2] and Cooke.[1] The sequence-to-series transformation has been defined by Hill.[3] The products, taken two by two, of some of the above matrices have been studied by Vermes.[5-7] In Sections 3 and 4 of this paper, I have considered the remaining cases of the products. As a consequence of this, I prove that the matrices defining convergence preserving sequence-to-series transformations form a Banach algebra under a suitable norm. Also, in Section 5, I prove two simple sufficient conditions for a suitably restricted sequence-to-series method to include or be equivalent with another of a similar type.

2. *Notations and known theorems.*—I shall briefly recall the various definitions and theorems proved on the products of these matrices.

We shall denote by (c) the *space of convergent sequences*, by (c_0) the *space of null sequences*, by (γ) the *space of convergent series* and by (γ_0) the *space of convergent series with sum zero*. The matrix $A \equiv a_{nk}$ transforming the ' points ' of the space (X) into those of (Y) shall be, for brevity, denoted by $A \subset \Gamma(X, Y)$.

The standard method of summing a series $u_0 + u_1 + u_2 + \ldots\ldots\ldots$ with partial sums $\{s_k\}$, $s_k = u_0 + u_1 + \ldots + u_k$ is the *transformation of the sequence* $\{s_k\}$ by the matrix $A \equiv a_{nk}$ *into a* convergent *sequence* $\sigma_n = \sum_k a_{nk} s_k$. The matrix A is said to be convergence preserving or simply a *K-matrix* if the convergence of $\{s_k\}$ implies that of $\{\sigma_n\}$. If in addition the limit is also preserved then the transformation is said to be regular and the matrix a *T-matrix*. The matrix is said to be " *multiplicative* ρ " or simply $\subset \Gamma(c, \rho c)$

if $\lim s_k = l$ implies $\lim \sigma_n = \rho . l$. The necessary and sufficient conditions that the matrix A is a *K*-matrix are (Dienes[3], p. 388)

$$(2.1.1)\quad \sum_k |\, a_{nk} \,| \leqslant \mathrm{M}, \text{ a quantity independent of } n,$$

$$(2.1.2)\quad \lim_n a_{nk} = \delta_k \text{ exists for each } k,$$

and $$(2.1.3)\quad \gamma_n = \sum_k a_{nk} \to \gamma \text{ as } n \to \infty.$$

The necessary and sufficient conditions that A is " multiplicative ρ " are that $\delta_k \equiv 0$ and $\gamma = \rho$; consequently A is a *T*-matrix if and only if, $\delta_k \equiv 0$, $\gamma = 1$. Conditions (2.1.1) and (2.1.2) above are necessary and sufficient for A to be $\subset \Gamma(c_0, c)$ while (2.1.1) and (2.1.2) with $\delta_k \equiv 0$ are necessary and sufficient for A to be $\subset \Gamma(c_0, c_0)$. The matrix A satisfying condition (2.1.1) shall be called a *K_r-matrix*.

Another method is the *transformation of the series* $\sum_k u_k$ *into a* convergent *sequence* $t_n = \sum_k f_{nk} u_k$ by a matrix $\mathrm{F} \equiv f_{nk}$. A convergence preserving series-to-sequence transformation matrix is called a *β-matrix* while the limit preserving one is called a *γ-matrix*. The necessary and sufficient conditions that F may be a *β-matrix* are:

$$(2.2.1)\quad \sum_k |\, f_{nk} - f_{n,\,k+1} \,| \leqslant \mathrm{M}, \text{ a quantity independent of } n.$$

and $$(2.2.2)\quad \lim_n f_{nk} = \beta_k \text{ exists for each } k.$$

The matrix F will be a γ-matrix if, and only if, in addition $\beta_k \equiv 1$ and F will be $\subset \Gamma(\gamma, c_0)$ if $\beta_k \equiv 0$.

A third method is the *transformation of the series* $\sum_k u_k$ by the matrix $\mathrm{H} \equiv h_{nk}$ *into a* convergence *series* $\sum v_n$, so that $v_n = \sum_k h_{nk} u_k$. A convergence preserving transformation of this type is said to be defined by a *δ-matrix* and a limit preserving one by an *α-matrix*. The necessary and sufficient condition that the matrix H is a δ or an α-matrix is that the matrix F defined by

$$(2.3)\quad f_{nk} = h_{0k} + h_{1k} + \ldots + h_{nk} \text{ or } h_{nk} = f_{nk} - f_{n-1,\,k}$$

is a β-matrix or a γ-matrix, respectively (Vermes[6, 7]).

The sequence-to-series transformation, defined by Hill,[3] consists in *transforming a sequence* $\{s_k\}$ *into a* convergent *series* $\sum_n v_n$ by a matrix $\mathrm{P} \equiv p_{nk}$ so that $v_n = \sum_k p_{nk} s_k$. We define a matrix yielding a convergence preserving

transformation of this type to be a *λ-matrix* while the limit preserving one is called a *μ-matrix*. The necessary and sufficient condition for the matrix P to be a λ-matrix or a μ-matrix is that the matrix A defined by

(2.4) $a_{nk} = p_{0k} + p_{1k} + \ldots + p_{nk}$ or $p_{nk} = a_{nk} - a_{n-1,k}$

is a *K*-matrix or a *T*-matrix, respectively (Hill[3]).

From the definitions and properties mentioned above, we have also

THEOREM 2.5: *Every δ-matrix is also a β-matrix and indeed* $\subset \Gamma(\gamma, c_0)$.

Also, in a λ-matrix P, we have, if A is the corresponding *K*-matrix then

$$\sum_k |p_{nk}| = \sum_k |a_{nk} - a_{n-1,k}| \leq \sum_k |a_{nk}| + \sum_k |a_{n-1,k}| \leq 2M,$$

$\lim_n p_{nk} \equiv 0$, since $\lim_n a_{nk}$ exists.

Also,

$$\sum_k p_{nk} = \sum_k (a_{nk} - a_{n-1,k}) = \gamma_n - \gamma_{n-1}$$

and therefore

$$\lim_n \sum_k p_{nk} = 0.$$

Thus we have

THEOREM 2.6: *Every λ-matrix is a multiplicative zero matrix; i.e.,* $\subset \Gamma(c, c_0)$.

Several theorems on the products of the matrices have been proved earlier and we shall briefly state them here for the sake of completeness.

THEOREM 2.7: *The product C = AB of two K-matrices is a K-matrix.*

THEOREM 2.8: *The product C = AF of a β-matrix F with a matrix A exists and is a β-matrix if, and only if, A is a K-matrix.*

THEOREM 2.9: *The product C = AF of a γ-matrix F with a matrix A exists and is a γ-matrix if, and only if, A is a T-matrix.*

THEOREM 2.10: *The product C = FA of a γ-matrix F and a T-matrix A need not exist.*

THEOREM 2.11: *The product C = FH of any β-matrix F with a matrix H exists and is a β-matrix if, and only if, H is a δ-matrix.*

THEOREM 2.12. *The product C = FH of any γ-matrix F with a matrix H exists and is a γ-matrix if, and only if, H is an α-matrix.*

THEOREM 2.13: *The product C = GF of two β-matrices G and F need not exist.*

THEOREM 2.14: *The product $C = HF$ of an α-matrix H with a γ-matrix F need not exist.*

THEOREM 2.15: *The product of two δ-matrices is a δ-matrix.*

THEOREM 2.16: *The product of two α-matrices is an α-matrix.*

THEOREM 2.7 is well known and its proof can be found in Cooke.[1]

THEOREMS 2.8–2.16 are due to Vermes[5–7].

3. In this section I shall prove some preliminary theorems on the products of summability matrices.

We have in virtue of the various necessary and sufficient conditions stated earlier, the following relationships between the various summability matrices.

$$\mu \subset \lambda \subset \Gamma(c, c_0) \subset K \subset \beta \text{ and } \alpha \subset \delta \subset \Gamma(\gamma, c_0) \subset \beta.$$

Also, from the way the λ and δ-matrices are formed out of their corresponding K and β-matrices we have, from the relation $K \subset \beta$ that $\lambda \subset \delta$. But $\mu \not\subset \alpha$ since $T \not\subset \gamma$.

THEOREM 3.1: *Let $A \subset \Gamma(c, \rho c)$ and $B \subset \Gamma(c, \rho' c)$. Then the product $C = AB$ is $\subset \Gamma(c, \rho\rho' c)$.*

Proof.—It follows from the hypothesis that, since both A and B are K_r-matrices, so is their product C.

Now, $c_{nk} = \sum_i a_{ni} b_{ik}$ and therefore for each fixed k, $\{c_{nk}\}$ can be regarded as the A-transform of the sequence $\{b_{ik}\}$.

But, since $\{b_{ik}\}$ is a null sequence, by hypothesis, and also since $A \subset \Gamma(c, \rho c)$ we have that $\lim_n c_{nk} = 0$, for each fixed k.

Further, $\sum_k c_{nk} = \sum_k \sum_i a_{ni} b_{ik}$.

Since A and B are K_r-matrices, we have that $\sum_k \sum_i |a_{ni}| \cdot |b_{ik}| < \infty$.

Therefore we have, on the interchange of the order of summation,

$$\sum_k c_{nk} = \sum_i \sum_k a_{ni} b_{ik} = \sum_i a_{ni} \sum_k b_{ik} = \sum_i a_{ni} \gamma_i', \text{ say.}$$

But since $B \subset \Gamma(c, \rho' c)$, $\gamma_i' \to \rho'$ as $i \to \infty$.

$\sum_k c_{nk}$ can now be regarded as the A-transform of the sequence (γ_i') and consequently we have that $\lim_n \sum_k c_{nk} = \rho . \rho'$.

This completes the proof of the theorem.

THEOREM 3.2: *The product $C = AH$ of a K-matrix A and a δ-matrix H is a β-matrix.*

The conclusion of the theorem is seen to be true immediately from Theorem 2.6, since every δ-matrix is also a β-matrix, by theorem 2.5. Now, we shall prove that the conclusion is the "*best possible*", in the sense that it need be only a β and not necessarily a K- or a δ-matrix, since it is likely that a β-matrix may be a K- or a δ-matrix. This is seen by taking

$$A = \begin{vmatrix} 1\ 0\ 0 \ldots\ldots\ldots \\ 1\ 0\ 0 \ldots\ldots\ldots \\ 1\ 0\ 0 \ldots\ldots\ldots \\ \ldots\ldots\ldots\ldots \\ \ldots\ldots\ldots\ldots \end{vmatrix} \quad \text{and } H = \begin{vmatrix} 1\ 1\ 1 \ldots\ldots\ldots \\ 0\ 0\ 0 \ldots\ldots\ldots \\ 0\ 0\ 0 \ldots\ldots\ldots \\ \ldots\ldots\ldots\ldots \\ \ldots\ldots\ldots\ldots \end{vmatrix}$$

so that

$$AH = \begin{vmatrix} 1\ 1\ 1 \ldots\ldots\ldots \\ 1\ 1\ 1 \ldots\ldots\ldots \\ \ldots\ldots\ldots\ldots \\ \ldots\ldots\ldots\ldots \end{vmatrix}$$

which is neither a K- nor a δ-matrix.

NOTE.—For the product C to be a β-matrix for every K-matrix A, it is not necessary that H should be a δ-matrix, since by Theorem 2.8 it is enough if it is a β-matrix.

THEOREM 3.3: *The product $C = HA$ of a δ-matrix H with a K-matrix A need not exist.*

This can be directly verified by taking the matrices A and H as in the previous theorem.

THEOREM 3.4: *The product $C = AH$ of the matrix $A \subset \Gamma(c, \rho c)$ and δ-matrix H is $\subset \Gamma(\gamma, c_0)$.*

Proof.—Since any multiplicative matrix is also a K-matrix it follows from Theorem 3.2 that the product matrix C is at least a β-matrix. Now, it is enough if we prove that $\lim_n c_{nk} \equiv 0$. This is evident since, as before, we can regard the sequence $\{c_{nk}\}$ for each fixed k, as the A-transform of the sequence $\{h_{ik}\}$, regarded as a sequence in i, which in the present case happens

to be a null sequence on account of the convergence of $f_{nk} = h_{0k} + h_{1k} + \ldots + h_{nk}$ as $n \to \infty$ and also since the matrix A is multiplicative.

COROLLARY: *The product $C = AH$ of a T-matrix A and an α-matrix* H is $\subset \Gamma(\gamma, c_0)$.

That the product need not be a δ-matrix can be seen by taking for A the (C, 1) matrix and H, the Identity Matrix, so that the product is still the (C, 1) matrix, which is not a δ-matrix. Thus the conclusion is the "*best possible*".

4. *λ and μ-matrices.*—In this section we shall consider the products of the various matrices with the λ or μ-matrices, either to the left or to the right.

THEOREM 4.1: *The product $C = PA$ of a λ-matrix P with a matrix A exists and is a λ-matrix if, and only if, A is a K-matrix.*

Proof.—Let B be the *K*-matrix corresponding to the λ-matrix P,

so that $b_{nk} = p_{0k} + p_{1k} + \ldots + p_{nk}$ or $p_{nk} = b_{nk} - b_{n-1,k}$.

Now $c_{nk} = \sum_i p_{ni}\, a_{ik} = \sum_i (b_{ni} - b_{n-1,i})\, a_{ik} = [BA]_{nk} - [BA]_{n-1,k}$.

But since B and A are *K*-matrices, so is their product BA, and therefore it follows that C is a λ-matrix. Thus the condition is sufficient. That the condition is necessary is seen by taking

$$P = \begin{vmatrix} 1 & 0 & 0 & 0\ldots\ldots \\ -1 & 1 & 0 & 0\ldots\ldots \\ 0 & -1 & 1 & 0\ldots\ldots \\ 0 & 0 & -1 & 1\ldots\ldots \\ \ldots\ldots\ldots\ldots\ldots\ldots \\ \ldots\ldots\ldots\ldots\ldots\ldots \end{vmatrix}$$ and any matrix A.

Then $c_{nk} = a_{nk} - a_{n-1,k}$.

Now, if C is to be a λ-matrix, then A must be a *K*-matrix.

The above proof also gives rise to

THEOREM 4.2: *The product $C = PA$ of a μ-matrix P with any matrix A exists and is a μ-matrix if, and only if, A is a T-matrix.*

THEOREM 4.3: *The product $C = AP$ of any K-matrix A with a λ-matrix P is a K-matrix.*

The result follows from the fact that every λ-matrix is also a *K*-matrix and Theorem 2.7.

We shall also prove that the above conclusion is the '*best possible*' by proving that the product need not be a λ-matrix. This will follow by taking for A the matrix A of Theorem 3.2 and P any arbitrary λ-matrix. Then,

$$C = \begin{vmatrix} p_{00} & p_{01} \cdots p_{0k} \cdots \cdots \\ p_{00} & p_{01} \cdots p_{0k} \cdots \cdots \\ \cdots\cdots\cdots\cdots\cdots \\ \cdots\cdots\cdots\cdots\cdots \end{vmatrix}$$

and this cannot be a λ-matrix, unless $\{p_{nk}\}$ are all zero.

Remark 1.—The product C = AP of the matrix $A \subset \Gamma(c, \rho c)$ and a λ-matrix P is $\subset \Gamma(c, c_0)$.

This is a consequence of the fact that every λ-matrix is $\Gamma(c, c_0)$ and Theorem 3.1.

From Remark 1, it follows that

Remark 2.—*The product C = AP of a T-matrix A and a μ-matrix P is* $\subset \Gamma(c, c_0)$ *and therefore cannot be a T-matrix.*

Remark 3.—In order that the product C = AP of any *K*-matrix A with a matrix P may be a *K*-matrix it is not necessary that P should be a λ-matrix, since by Theorem 2.7 it is enough if it is a *K*-matrix.

Remark 4.—In order that the product C = AP may be a *K*-matrix for any arbitrary λ-matrix P and a matrix A it is not necessary that A should be a *K*-matrix as may be seen by taking for A the matrix

$$\begin{vmatrix} 1 & 1 & 1 \cdots\cdots \\ 1 & 1 & 1 \cdots\cdots \\ 1 & 1 & 1 \cdots\cdots \\ \cdots\cdots\cdots\cdots \\ \cdots\cdots\cdots\cdots \end{vmatrix}$$

Then $c_{nk} = \sum_i a_{ni} p_{ik} = \sum_i p_{ik} = \delta_k$ say, where δ_k is the quantity $\lim_i b_{ik}$ when B is the *K*-matrix corresponding to the λ-matrix P. Now the result follows from the fact that for any *K*-matrix $\sum_k |\delta_k| < \infty$.

THEOREM 4.4: *The product of two λ-matrices P and Q is also a λ-matrix.*

Proof.—Let A be the *K*-matrix corresponding to the λ-matrix P defined by the equation (2.4). Then, we have, if C = PQ

$$c_{nk} = \sum_i p_{ni} q_{ik} = \sum_i (a_{ni} - a_{n-1,i})\, q_{ik} = [AQ]_{nk} - [AQ]_{n-1,k}$$

and AQ is by Theorem 4.3 a *K*-matrix. Therefore the result follows. From Remark 2 to Theorem 4.3 we have,

THEOREM 4.5: *The product of two μ-matrices P and Q is* $\subset \Gamma(c, \gamma_0)$ *and cannot be a μ-matrix.*

THEOREM 4.6: *The product C = PF of a λ-matrix P with a matrix F is a δ-matrix if, and only if, F is a β-matrix.*

The result is a consequence of the fact that if A is the *K*-matrix corresponding to the λ-matrix P and D = AF then $d_{nk} = c_{0k} + c_{1k} + \ldots + c_{nk}$. Now C is a δ-matrix if, and only if, D is a β-matrix, which happens by Theorem 2.8 if and only if F is a β-matrix, since by hypothesis A is a *K*-matrix.

A similar argument shows that

THEOREM 4.7: *The product C = PF of a μ-matrix P with a matrix F is an α-matrix if, and only if, F is a γ-matrix.*

THEOREM 4.8: *The product C = PH of a λ-matrix P with a δ-matrix H is a δ-matrix.*

Proof.—Let A be the *K*-matrix corresponding to the λ-matrix P. Then as before, $c_{nk} = [AH]_{nk} - [AH]_{n-1,k}$.

Now, AH is by Theorem 3.2, a β-matrix and therefore we have that C is a δ-matrix.

It may be remarked here also that in order that the product C = PH of a matrix P with a δ-matrix H may be a δ-matrix it is not necessary that P should be a λ-matrix, since we have by Theorem 2.15 that it is enough if it is a δ-matrix.

After the Corollary to Theorem 3.4 we have also the following:

THEOREM 4.9: *The product C = PH of any μ-matrix P and an α-matrix H is* $\subset \Gamma(\gamma, \gamma_0)$.

Next we prove the following theorem.

THEOREM 4.10: *The product C = FP of a β-matrix F with a λ-matrix P is a matrix* $\subset \Gamma(c_0, c)$.

Proof.—Since every λ-matrix is also a *K*-matrix, we have, after Theorem 2.11 that C is a β-matrix; *i.e.*, that each column of the matrix C is convergent.

Now if A is the *K*-matrix corresponding to the λ-matrix P, we have

$$c_{nk} = \sum_i f_{ni} p_{ik}$$

$$= \sum_i f_{ni} (a_{ik} - a_{i-1,k}) = \sum_i (f_{ni} - f_{n,i+1}) a_{ik} + \lim_i (f_{ni} a_{ik}).$$

Therefore, we have

$$\sum_k | c_{nk} | \leqslant \sum_k | \sum_i (f_{ni} - f_{n,i+1}) a_{ik} | + \sum_k | \lim_i (f_{ni} a_{ik}) |$$

But since F is a β-matrix, we have that $\{f_{ni}\}$ are bounded, regarded as sequences in n or i (Vermes[5]).

Therefore,

$$\sum_k | c_{nk} | \leqslant \sum_k \sum_i | f_{ni} - f_{n,i+1} | \ | a_{ik} | + \sum_k \mathbf{M} | \delta_k |$$

where M is the upper bound of the sequence $\{f_{ni}\}$ regarded as a sequence in i and $\lim_i a_{ik} = \delta_k$.

Since now in a *K*-matrix $\sum_k | \delta_k | < \infty$ we have that $\sum | c_{nk} | < \infty$, for each n, since F is a β-matrix and A is a *K*-matrix.

Thus the product C is also a K_τ-matrix. Now the conclusion in the theorem follows from C being simultaneously β and K_τ.

THEOREM 4.11: *The product C = FP of a γ-matrix F and a μ-matrix P is a matrix* $\subset \Gamma(c_0, c_0)$.

Proof.—In the light of the proof of Theorem 4.10, we have only to show that $\lim_n c_{nk} \equiv 0$. This is obvious since $\{c_{nk}\}$ can be regarded as the F-transform of the series $\sum_i p_{ik}$ which by the property of the μ-matrix is a series with sum zero.

Theorems 4.10 and 4.11 give rise to the following two theorems:

THEOREM 4.12: *The product C = HP of a δ-matrix H with a λ-matrix P is a matrix* $\subset \Gamma(c_0, \gamma)$.

THEOREM 4.13: *The product C = HP of an α-matrix H with a μ-matrix P is a matrix* $\subset \Gamma(c_0, \gamma_0)$.

THEOREM 4.14: *The set of λ-matrices P form a Banach Algebra under the norm* $\| P \| = 2.l.u.b._n \sum_{k=0}^{\infty} | \sum_{i=0}^{n} p_{ik} |$

Proof.—Let $P^r \equiv [p^r{}_{ik}]$ be a sequence of λ-matrices.

Then $P^r.P^s$ and $P^r + P^s$ are λ-matrices is evident.

Therefore we have only to prove that the space of the above matrices is complete under the norm specified and that $\| P^r.P^s \| \leqslant \|P^r\|.\| P^s\|$. First we prove the completeness of the space, *i.e.*, that each Cauchy sequence in the space implies the existence of a member of the space to which that sequence will converge.

Now, let $\| P^r - P^s \| \leqslant \epsilon,\ r, s \geqslant n_0$.

That the above condition is necessary for the convergence of $\{P^r\}$ is clear. To prove that it is also sufficient, let A^r denote the K-matrix corresponding to the λ-matrix P^r.

Now, given a matrix $D = [d_{ik}]$, let $\| D \|_\lambda$ denote $2.\underset{n}{l.u.b} \sum_k | \sum_{i=0}^{n} d_{ik} |$

and let $\| D \|_k$ denote $\underset{n}{l.u.b} \sum_k | d_{nk} |$.

Then we have that $\| P^r \|_\lambda = 2 \| A^r \|_k$

Now, $\| P^r - P^s \|_\lambda = 2 \| A^r - A^s \|_k \leqslant \epsilon,\ r, s \geqslant n_0$.

Since $\| A^r - A^s \|_k \leqslant \epsilon/2,\ r, s \geqslant n_0$ and the K-matrices form a Banach Algebra under the norm $\| A \|_k$* we have that there exists a K-matrix A to which the sequence of matrices A^r converge. Corresponding to this K-matrix A there exists a λ-matrix P which is the limit of the sequence P^r. Thus the space is complete under the norm chosen and indeed complete under the norm $\| P \| = \underset{n}{l.u.b} \sum_k | \sum_{i=0}^{n} p_{ik} |$

To prove that $\| P^r.P^s \|_\lambda \leqslant \| P^r \|_\lambda \cdot \| P^s \|_\lambda$,

let $C = P^r.P^s$, *i.e.*, $c_{nk} = \sum_i p^r{}_{ni} \cdot p^s{}_{ik}$.

Let $B \equiv (b_{nk})$ where $b_{nk} = c_{0k} + c_{1k} + \ldots + c_{nk}$

i.e., $B = A^r.P^s$.

Now, since A^r is a K-matrix and the matrix P^s is a λ-matrix and therefore necessarily a K-matrix we have that B is a K-matrix and therefore

$$\| B \|_k \leqslant \| A^r \|_k \cdot \| P^s \|_k$$

and consequently $\| C \|_\lambda = 2 \| B \|_k \leqslant 2 \| A^r \|_k \cdot \| P^s \|_k = \| P^r \|_\lambda \cdot \| P^s \|_k$.

* This result is due to Parameswaran[4] (Theorem I).

Now, $\| P^s \|_k = l.u.b_n \sum_k | p^s{}_{nk} |$

$= l.u.b_n \sum_k | a^s{}_{nk} - a^s{}_{n-1,k} |$

$\leq l.u.b_n \sum_k | a^s{}_{nk} | + l.u.b_n \sum_k | a^s{}_{n-1,k} | = 2 \| A^s \|_k = \| P^s \|_\lambda.$

Therefore $\| C \|_\lambda \leq \| P^r \|_\lambda \cdot \| P^s \|_\lambda$

and this completes the proof of the theorem.

Remark.—On account of the 1–1 correspondence between the λ-matrices P^r and the K-matrices A^r defined by the relation

$$a^r{}_{nk} = p^r{}_{0k} + p^r{}_{1k} + \ldots + p^r{}_{nk}$$

and the fact that the K-matrices form a Banach Algebra under the norm $\| A \|_k$ it is natural to expect that the λ-matrices will form a Banach Algebra under the corresponding K-norm. But that they do not do so can be seen from the example below. Suppose we have $\| P \|_\lambda = \| A \|_k$

Let

$$P^r = P^s = \begin{vmatrix} 1 & 0 & 0 & 0\ldots. \\ -1 & 1 & 0 & 0\ldots. \\ 0 & -1 & 1 & 0\ldots. \\ 0 & 0 & -1 & 1\ldots. \\ \ldots\ldots\ldots\ldots\ldots \end{vmatrix}$$

so that $A^r = A^s = I$, identity matrix

In the notation of the proof of the theorem we have, $D = P^s$.

Therefore $\| D \|_k = \| P^s \|_k = 2$.

But $\| A^r \|_k = 1$ and therefore $\| D \|_k \geq \| A^r \|_k \cdot \| A^s \|_k$, *i.e.*,

$$\| C \|_\lambda \geq \| P^r \|_\lambda \cdot \| P^s \|_\lambda.$$

5. *Inclusion Theorems.*—In this section we obtain a necessary and sufficient condition for a sequence-to-series transformation method defined by a suitably restricted μ-matrix P to include another similar method, given by a matrix Q. Also a sufficient condition for the inclusion of one method in the other is proved.

Definitions.—Let $\{s_k\}$ be any sequence, convergent or not, and let P and Q be two μ-matrices. If the existence of the P-limit of the sequence $\{s_k\}$ implies the existence and its equality with the Q-limit of the sequence then the method *Q is said to include the method P* and this is denoted by $Q \supset P$. If in addition $P \supset Q$, then the methods are said to be *equivalent* and this is denoted by $P \sim Q$.

THEOREM 5.1: *Let P and Q be two row-finite μ-matrices and let P have a left-hand row-finite reciprocal $^{-1}$P. Then $Q \supset P$ if, and only if, ^{-1}P is a γ-matrix.*

Proof.—Let $\{s_k\}$ be any sequence.

Let $v_n = \sum_k p_{nk} s_k$ and $\sum v_n = l$, say.

Now, since P has a left-hand row-finite reciprocal $^{-1}$P, we have

$$s_m = \sum_n {}^{-1}p_{mn}\, v_n.$$

If now $\sum_i u_i$ is the Q-transform of the sequence $\{s_k\}$ we have,

$$u_i = \sum_m q_{im}\, s_m = \sum_m q_{im} \sum_n {}^{-1}p_{mn}\, v_n.$$

Since Σv_n converges and Q and $^{-1}$P are row-finite, we have on the interchange of the order of summation of the above expression that the series $\sum_i u_i$ is the (Q.$^{-1}$P) transform of the series Σv_n. Therefore, if now, we must have that $Q \supset P$, *i.e.*, $\Sigma u_i = \Sigma v_n = l$ then the matrix (Q.$^{-1}$P) must be an α-matrix. But since Q is a μ-matrix, it follows from Theorem 4.7 that Q.$^{-1}$P will be an α-matrix if, and only if, $^{-1}$P is a γ-matrix and this completes the proof of the theorem.

COROLLARY: *Let the μ-matrices P and Q with their left-hand reciprocals ^{-1}P and ^{-1}Q (supposed to be existent) be row-finite. Then $P \sim Q$ if, and only if both $^{-1}$P and ^{-1}Q are γ-matrices.*

Even if we do not assume the existence of the reciprocals, we can still proceed as follows to find a sufficient condition for $Q \supset P$. Let $\{s_k\}$ be any sequence and $v_n = \sum_k p_{nk} s_k$. Let $\Sigma v_n = l$, say.

Now take the transformation Σu_m of the series Σv_n by an α-matrix, H, say.

Then $$u_m = \sum_n h_{mn}\, v_n = \sum_n h_{mn} \sum_k p_{nk} s_k.$$

If both H and P are row-finite then the interchange of the order of the above summation will be valid and we will have that Σu_m is the transform of the sequence $\{s_k\}$ by the matrix HP.

Therefore, if we have that Q = HP then we have that $Q \supset P$.

Thus we have the

THEOREM 5.2: *If P and Q are two row-finite μ-matrices and there exists a row-finite α-matrix H such that $Q = HP$ then $Q \supset P$.*

COROLLARY: *If P and Q are two row-finite μ-matrices and there exist two row-finite α-matrices H and H' such that $Q = HP$ and $P = H'Q$ then $P \sim Q$.*

I would like to draw the attention of the reader to the table I have given in the Appendix, which gives a complete picture of the existence and the classification of the various products considered in this paper and by the previous authors as well.

In conclusion I have very great pleasure in recording my indebtedness to Professor C. T. Rajagopal and Professor V. Ganapathy Iyer for their help and guidance in the preparation of this paper.

Note.—I learn from Dr. P. Vermes of the University of London that Mr. F. Gerrish of that University has obtained independently results similar to those in this paper. I am grateful to Dr. Vermes for drawing my attention to the work of Mr. Gerrish.

APPENDIX

↗	K	β	δ	λ
K	K [1]	β [5]	β (3·2)	K (4·3)
β	need not exist [5]	need not exist [6]	β [7]	$\Gamma(C_0, C)$ (4·10)
δ	need not exist (3·3)	need not exist [6]	δ [7]	$\Gamma(C_0, \gamma)$ (4·12)
λ	λ (4·1)	δ (4·6)	δ (4·8)	λ (4·4)

↗	T	γ	α	μ
T	T [1]	γ [5]	$\Gamma(\gamma, C_0)$ (3·4)	$\Gamma(C, C_0)$ (4·3)
γ	need not exist [5]	need not exist [6]	γ [6]	$\Gamma(C_0, C_0)$ (4·11)
α	need not exist (3·3)	need not exist [6]	α [6]	$\Gamma(C_0, \gamma_0)$ (4·13)
μ	μ (4·2)	α (4·7)	$\Gamma(\gamma, \gamma_0)$ (4·9)	$\Gamma(C, \gamma_0)$ (4·5)

The above table gives the complete picture of the existence and the classification of the various products considered in this paper and also by the previous authors. The numbers in the brackets ( ) refer to the theorem in this paper where the result is proved, while the numbers in the brackets [ ] refer to the literature cited at the end of the paper. The product of any two matrices can be found out immediately from the table above.

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HYPO-ELASTIC PURE FLEXURE

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1. Introduction

In hypo-elasticity, a subject of very recent origin, Truesdell[1] has generalised the classical linear theory of elasticity by taking the stress increment as a function of small strain from the immediately preceding state. Mathematically speaking his constitutive equation is

$$\text{Rate of stress} = \text{F (Rate of deformation)}. \tag{1.1}$$

For the rate of stress he takes, to be dynamically consistent, the tensor

$$\tilde{S}_j{}^i \equiv \frac{\partial}{\partial t} S_j{}^i + S_j{}^i v^k{}_{,\,k} - S^{ik} v_{j,\,k} - S_j{}^k v^i{}_{,\,k} + S_j{}^i v^k{}_{,\,k}, \tag{1.2}$$

where $S_j{}^i$ is the spatial stress tensor referred for convenience to twice the shear modulus as the unit of stress, v^i, the velocity, comma, the covariant derivative; and for the rate of deformation

$$d_{ij} = \tfrac{1}{2}\,[v_{i,\,j} + v_{j,\,i}].$$

In a subsequent communication, (Truesdell[2]), he takes a still more general concept of elasticity by writing the constitutive equation of the ideal material as $\tilde{S} = F(d, S)$, where response to deformation d is moderated by reigning stress field S. Assuming that no modulus of the ideal material shall carry a dimension independent of the dimension of stress and that F is an analytic function of the components $d_j{}^i$ and $S_j{}^i$, he establishes the following differential equations for an hypo-elastic isotropic body:

$$\begin{aligned}\tilde{S} = {} & \delta g_0 1 + g_1 d + \delta g_2 S + M g_3 1 + \tfrac{1}{2} g_4 (dS + Sd) \\ & + \delta g_5 S^2 + M g_6 S + N g_7 1 + \tfrac{1}{2} g_8 (dS^2 + S^2 d) \\ & + M g_9 S^2 + N g_{10} S + N g_{11} S^2,\end{aligned}$$

where g's being dimensionless analytic functions of the principal invariants of S, and for different grades, g's being defined in a particular problem.

2. Here three equations of motion and one equation of mass have to be taken as in the classical theory of elasticity. Boundary conditions are also the same. The most important and interesting feature of the above non-linear theory is that the stress-strain relations are not assumed. Truesdell[2] has already discussed problems on simple shear and torsion.

3. In this paper, we propose to discuss the steady bending of a narrow but thick rectangular plate of constant density into a region of circular form of inner radius 'a' and outer radius 'b' assuming the material to be hypo-elastic and isotropic of grade zero. When the compressible material reduces to an incompressible one, it is interesting to find that the solution is independent of the assumption of the stress-strain relations. The results obtained here are found to be identical with those obtained by Seth[3] in which the assumption of stress-strain relations is involved.

4. For an isotropic hypo-elastic body of grade zero, we have:

$$g_0 \equiv \frac{\lambda}{2\mu},\ g_1 \equiv 1,\ g_2 \equiv g_3 \equiv g_4 \equiv \ldots\ldots \equiv g_{11} = 0, \text{ for all S.}$$

In cylindrical system of co-ordinates, the six constitutive differential equations of hypo-elasticity for a body of grade zero and of constant density ρ reduce to

$$\left[\frac{\partial}{\partial t} + u\frac{\partial}{\partial r} + v\frac{\partial}{\partial \theta} + w\frac{\partial}{\partial z}\right] S_r^{\ r} - 2S_r^{\ r}\frac{\partial u}{\partial r} - 2S_z^{\ r}\frac{\partial u}{\partial z} - S_\theta^{\ r}\left(1 + \frac{1}{r^2}\right)\frac{\partial u}{\partial \theta} = \frac{\partial u}{\partial r}, \tag{4.1}$$

$$\left[\frac{\partial}{\partial t} + u\frac{\partial}{\partial r} + v\frac{\partial}{\partial \theta} + w\frac{\partial}{\partial z}\right] S_\theta^{\ r} - S_\theta^{\ r}\left(\frac{2u}{r} + \frac{\partial v}{\partial \theta} + \frac{\partial u}{\partial r}\right) - S_\theta^{\ \theta}\frac{\partial u}{\partial \theta} - S_r^{\ r} r^2\frac{\partial v}{\partial r} - S_z^{\ r} r^2\frac{\partial v}{\partial z} - S_z^{\ \theta}\frac{\partial u}{\partial z} = \tfrac{1}{2}\left[\frac{\partial u}{\partial \theta} + r^2\frac{\partial v}{\partial r}\right], \tag{4.2}$$

$$\left[\frac{\partial}{\partial t} + u\frac{\partial}{\partial r} + v\frac{\partial}{\partial \theta} + w\frac{\partial}{\partial z}\right] S_z^{\ r} - S_z^{\ \theta}\frac{\partial u}{\partial \theta} - S_z^{\ z}\frac{\partial u}{\partial z} - S_z^{\ r}\left(\frac{\partial w}{\partial z} + \frac{\partial u}{\partial r}\right) - S_\theta^{\ r}\frac{1}{r^2}\frac{\partial w}{\partial \theta} - S_r^{\ r}\frac{\partial w}{\partial r} = \tfrac{1}{2}\left[\frac{\partial u}{\partial z} + \frac{\partial w}{\partial r}\right], \tag{4.3}$$

$$\left[\frac{\partial}{\partial t}+u\frac{\partial}{\partial r}+v\frac{\partial}{\partial\theta}+w\frac{\partial}{\partial z}\right]S_\theta{}^\theta-S_\theta{}^r\frac{\partial v}{\partial r}(r^2+1)$$

$$-2S_\theta{}^\theta\left(\frac{u}{r}+\frac{\partial v}{\partial\theta}\right)-S_z{}^\theta(1+r^2)\frac{\partial v}{\partial z}=\left[\frac{u}{r}+\frac{\partial v}{\partial\theta}\right], \quad (4.4)$$

$$\left[\frac{\partial}{\partial t}+u\frac{\partial}{\partial r}+v\frac{\partial}{\partial\theta}+w\frac{\partial}{\partial z}\right]S_z{}^\theta-S_z{}^\theta\left(\frac{\partial w}{\partial z}+\frac{\partial v}{\partial\theta}\right)$$

$$-S_z{}^z\frac{\partial v}{\partial z}-S_\theta{}^r\frac{\partial w}{\partial r}-S_\theta{}^\theta\frac{1}{r^2}\frac{\partial w}{\partial\theta}-S_z{}^r\frac{\partial v}{\partial r}$$

$$=\tfrac{1}{2}\left[\frac{\partial v}{\partial z}+\frac{\partial w}{r^2\partial\theta}\right], \quad (4.5)$$

$$\left[\frac{\partial}{\partial t}+u\frac{\partial}{\partial r}+v\frac{\partial}{\partial\theta}+w\frac{\partial}{\partial z}\right]S_z{}^z-2S_z{}^z\frac{\partial w}{\partial z}-2S_z{}^r\frac{\partial w}{\partial r}$$

$$-S_\theta{}^z\frac{\partial w}{\partial\theta}\left(1+\frac{1}{r^2}\right)=\frac{\partial w}{\partial z}, \quad (4.6)$$

The three equations of motion in the absence of external forces reduce to

$$2\mu\left[\frac{\partial}{\partial r}S_r{}^r+\frac{1}{r}\frac{\partial}{\partial\theta}S_\theta{}^r+\frac{S_r{}^r-S_\theta{}^\theta}{r}+\frac{\partial}{\partial z}S_z{}^r\right]$$

$$=\rho\left[u\frac{\partial u}{\partial r}+v\left(\frac{\partial u}{\partial\theta}-rv\right)+w\frac{\partial u}{\partial z}\right], \quad (4.7)$$

$$2\mu\left[\frac{\partial}{\partial r}S_\theta{}^r+\frac{2}{r}S_\theta{}^r+\frac{1}{r}\frac{\partial}{\partial\theta}S_\theta{}^\theta+\frac{\partial}{\partial z}S_z{}^\theta\right]$$

$$=\rho\left[u\frac{\partial v}{\partial r}+v\frac{\partial v}{\partial\theta}+\frac{2uv}{r}+w\frac{\partial v}{\partial z}\right]r, \quad (4.8)$$

$$2\mu\left[\frac{\partial}{\partial r}S_z{}^r+\frac{1}{r}\frac{\partial S_z{}^\theta}{\partial\theta}+\frac{1}{r}S_z{}^r+\frac{\partial}{\partial z}S_z{}^z\right]$$

$$=\rho\left[u\frac{\partial w}{\partial r}+v\frac{\partial w}{\partial\theta}+w\frac{\partial w}{\partial z}\right], \quad (4.9)$$

The equation of continuity is

$$\frac{\partial u}{\partial r}+\frac{u}{r}+\frac{\partial v}{\partial\theta}+\frac{\partial w}{\partial z}=0. \quad (4.10)$$

In pure flexure, the shears $S_z^r = S_\theta^r = S_z^\theta = 0$, and we tentatively take S_r^r, S_θ^θ, S_z^z as functions of r only. Considering (4.1), we get:

$$u \frac{d}{dr} S_r^r = (1 + 2S_r^r) \frac{\partial u}{\partial r},$$

which gives:

$$u = \chi'(\theta) \sqrt{1 + 2S_r^r}, \tag{4.11}$$

where $\chi'(\theta)$ is any arbitrary function of θ. Considering (4.4), we have:

$$u \frac{d}{dr} S^\theta_\theta = (1 + 2S^\theta_\theta) \left(\frac{u}{r} + \frac{\partial v}{\partial \theta}\right),$$

or using (4.11),

$$\frac{\partial v}{\partial \theta} = \chi'(\theta) \sqrt{1 + 2S_r^r} \left[\frac{1}{1 + 2S_\theta^\theta} \frac{d}{dr} S_\theta^\theta - \frac{1}{r}\right],$$

or $v = \chi(\theta) \lambda(r) + F(r)$, where $F(r)$ is an arbitrary function of r only, and

$$\lambda(r) = \sqrt{1 + 2S_r^r} \left[\frac{1}{1 + 2S_\theta^\theta} \frac{d}{dr} S_\theta^\theta - \frac{1}{r}\right]. \tag{4.12}$$

From (4.8), we get:

$$0 = u \frac{\partial v}{\partial r} + v \frac{\partial v}{\partial \theta} + \frac{2uv}{r}.$$

Putting for u and v we get:

$$0 = \chi(\theta) \left[\sqrt{1 + 2S_r^r}\, \lambda'(r) + \{\lambda(r)\}^2 + \frac{2\lambda(r)}{r} \sqrt{1 + 2S_r^r}\right]$$

$$+ \left[F'(r) \sqrt{1 + 2S_r^r} + F(r) \lambda(r) + \frac{2F(r)}{r} \sqrt{1 + 2S_r^r}\right].$$

For this to hold, we must have:

$$\sqrt{1 + 2S_r^r}\, \lambda'(r) + \{\lambda(r)\}^2 + \frac{2\lambda(r)}{r} \sqrt{1 + 2S_r^r} = 0,$$

and

$$\sqrt{1 + 2S_r^r}\, F'(r) + F(r) \lambda(r) + \frac{2F(r)}{r} \sqrt{1 + 2S_r^r} = 0. \tag{4.13}$$

Thus we conclude that $F(r) \equiv A\lambda(r)$, for all r.

Hence

$$v = [\chi(\theta) + A]\,\lambda(r). \tag{4.14}$$

Considering (4.10), we have:

$$\chi'(\theta) \cdot \left[\frac{d}{dr} S_r{}^r \cdot \frac{1}{\sqrt{1 + 2S_r{}^r}} + \frac{\sqrt{1 + 2S_r{}^r}}{r} + \frac{\lambda(r)}{r}\right] + a = 0.$$

Hence a must be zero. Then either $\chi'(\theta) = 0$, which gives $u = 0$; and $S_r{}^r$ becomes indeterminate. Therefore we do not take

$$\chi'(\theta) = 0.$$

Or

$$\frac{d}{dr} S_r{}^r \cdot \frac{1}{\sqrt{1 + 2S_r{}^r}} + \frac{\sqrt{1 + 2S_r{}^r}}{r} + \frac{\lambda(r)}{r} = 0. \tag{4.15}$$

Considering (4.2), we get:

$$-\frac{\partial u}{\partial \theta}\left(S_\theta{}^\theta + \tfrac{1}{2}\right) = r^2 \frac{\partial v}{\partial r}\left(\tfrac{1}{2} + S_r{}^r\right),$$

or

$$\frac{-\chi''(\theta)\{2S_\theta{}^\theta + 1\}}{\{\chi(\theta) + A\}\sqrt{1 + 2S_\theta{}^\theta}} = -r^2\lambda'(r), \tag{4.16}$$

For this to hold we should have:

$$\chi''(\theta) = 0, \quad \chi'(\theta) = \text{constant}, \tag{4.17}$$

$$\therefore \quad \lambda'(r) = 0. \tag{4.17}$$

Using (4.13), we find:

$$\lambda(r)\left[\lambda(r) + \frac{2}{r}\sqrt{1 + 2S_r{}^r}\right] = 0.$$

$\therefore$ Either,

$$\lambda = 0,$$

or

$$\lambda = -\frac{2}{r}\sqrt{1 + 2S_r{}^r}. \tag{4.18}$$

If $\lambda = 0$, from (4.12), we get:

$$\frac{1}{1+2S_\theta{}^\theta} \cdot \frac{d}{dr} S_\theta{}^\theta - \frac{1}{r} = 0,$$

or

$$S_\theta{}^\theta = \frac{D^2}{2} \cdot r^2 - \tfrac{1}{2}, \tag{4.19}$$

where D is an arbitrary constant.

Also from (4.15), we get:

$$\frac{1}{\sqrt{1+2S_r{}^r}} \frac{d}{dr} S_r{}^r + \frac{\sqrt{1+2S_r{}^r}}{r} = 0,$$

$$\therefore \quad r\sqrt{1+2S_r{}^r} = D',$$

where D′ is an arbitrary constant

or

$$S_r{}^r = \frac{D'^2}{2r^2} - \tfrac{1}{2}. \tag{4.20}$$

In this case,

$$u = \sqrt{1+2S_r{}^r}\, \chi'(\theta) = \chi'(\theta) \frac{D'}{r},$$

where $\chi'(\theta)$ is a constant.

$v = 0$, and from (4.5), w is also zero. All other equations are satisfied except the equation (4.7), which gives

$$2\mu\left[-\frac{D'^2}{r^3} + \frac{D'^2}{2r^3} - \frac{D^2 r}{2}\right] = \rho\left[\{\chi'(\theta)\}^2 \cdot \frac{D'}{r} \cdot \left(-\frac{D'}{r^2}\right)\right];$$

this is possible only when $D = 0$ and then $\chi'(\theta) = \sqrt{\frac{\mu}{\rho}}$ (4.21)

If $\lambda = -\frac{2}{r}\sqrt{1+2S_r{}^r}$, refer to (4.18),

then (4·12) gives:

$$-\frac{2}{r} = \frac{1}{1+2S_\theta{}^\theta} \frac{d}{dr} S_\theta{}^\theta - \frac{1}{r},$$

or

$$-\frac{1}{r} = \frac{1}{1+2S_\theta{}^\theta}\frac{d}{dr}S_\theta{}^\theta,$$

or $-2\log r = \log(1+2S_\theta{}^\theta) - \log A'$, where A' is an arbitrary constant.

$$\therefore \quad S_\theta{}^\theta = \frac{A'}{2r^2} - \tfrac{1}{2}. \tag{4.22}$$

From (4.15),

$$\frac{d}{dr}S_r{}^r \cdot \frac{1}{\sqrt{1+2S_r{}^r}} + \frac{\sqrt{1+2S_r{}^r}}{r} - \frac{2}{r}\sqrt{1+2S_r{}^r} = 0,$$

or

$$\frac{d}{dr}S_r{}^r \frac{1}{\sqrt{1+2S_r{}^r}} = \frac{1}{r}\sqrt{1+2S_r{}^r}, \text{ or } S_r{}^r = \frac{B'^2}{2}r^2 - \tfrac{1}{2}, \tag{4.23}$$

where B' is an arbitrary constant.

From (4.7), we get:

$$2\mu\left[B'^2 r + \left\{\tfrac{1}{2}B'^2 r^2 - \frac{A'}{2r^2}\right\}\frac{1}{r}\right]$$
$$= \rho\left[\{\chi'(\theta)\}^2 rB'^2 - 2B'\{\chi(\theta)+A\}\chi''(\theta)rB'\right.$$
$$\left. - r\{\chi(\theta)+A\}^2 4B'^2\right],$$

which is not satisfied.

Thus we have the system of stresses and displacements:

$$S_r{}^r = \frac{D'^2}{2}\cdot\frac{1}{r^2} - \tfrac{1}{2},\ S_\theta{}^\theta = -\tfrac{1}{2},\ S_z{}^z = 0,\ S_\theta{}^r = S_z{}^\theta = S_r{}^z = 0;$$

$$u = \frac{D'}{r}\sqrt{\frac{\mu}{\rho}},\ v = 0,\ w = 0.$$

Taking the contravariant stress components, we find:

$$S^{rr} = \frac{D'^2}{2r^2} - \tfrac{1}{2},\ S^{\theta\theta} = -\frac{1}{2r^2},\ S^{zz} = 0,\ S^{r\theta} = S^{\theta z} = S^{zr} = 0.$$

Let us apply the boundary condition

$$S^{rr} = 0 \text{ at } r = a, \text{ which gives } D' = a.$$

Thus

$$S^{rr} = \frac{a^2}{2r^2} - \tfrac{1}{2}, \quad S^{\theta\theta} = -\frac{1}{2r^2}, \quad S^{zz} = 0,$$

$$S^{\theta z} = S^{rz} = S^{r\theta} = 0.$$

This shows that a traction must be applied to the straight edges and to one of the curved surfaces of the cylinder so as to keep the plate in circular form. The force which must be applied to the curved surface is

$$(S^{rr})_{r=b} = \frac{a^2}{2b^2} - \tfrac{1}{2}.$$

If M_1 denotes the moment of the couple about an axis perpendicular to the plane of the tube and passing through its centre,

$$M_1 = \int_a^b rs^{\theta\theta} dr = -\int_a^b r \frac{1}{2r^2} dr = -\tfrac{1}{2} \log \frac{b}{a}.$$

If $-M_2$ denotes the moment of the elementary couple in the axial plane applied to the plane ends of the cylinder between θ and $\theta + d\theta$, we must have:

$$\int_a^b rS^{zz}\, dr = 0, \quad \text{and} \quad -M_2 = 0,$$

which is true;

the traction across the plane $\theta =$ constant is

$$S^{\theta\theta} = -\frac{1}{2r^2}.$$

5. Seth[3] has discussed the pure flexure problem in the finite strain theory. By taking large strains and assuming the stress-strain relations he gets the same stresses as follows:

$$S^{rr} = \lambda + \mu + \frac{\mu A^2}{r^2} - \frac{(\frac{1}{2}\lambda + \mu)\, l}{r^c},$$

$$S^{\theta\theta} = \lambda + \mu - \frac{\mu A^2}{r^2} - \tfrac{1}{2}\frac{\lambda l}{r^c},$$

$$S^{r\theta} = S^{rz} = S^{\theta z} = S^{zz} = 0,$$

where

$$\mu A^2 = \frac{(\lambda + \mu)\,(ab)^{2-c}\,(a^c - b^c)}{a^{2-c} - b^{2-c}}, \tag{5.1}$$

and

$$(\tfrac{1}{2}\lambda + \mu)\, l = \frac{(\lambda + \mu)(a^2 - b^2)}{a^{2-c} - b^{2-c}}. \tag{5.2}$$

In the incompressible case, $\lambda \to \infty$, $c \to 0$, and using (5.2),

$$(\tfrac{1}{2} \cdot \lambda + \mu)\, l \to \lambda + \mu, \text{ } i.e., \text{ } l \to 2,$$

$$\therefore \quad S^{rr} = -\mu + \mu \frac{A^2}{r^2}, \quad S^{\theta\theta} = \mu - \mu \frac{A^2}{r^2},$$

$$S^{zz} = S^{r\theta} = S^{\theta z} = S^{zr} = 0.$$

Thus we find that our S^{rr} and his S^{rr} are the same, keeping in view the fact that we are taking twice the shear modulus as our unit. S^{zz} is zero in both cases. Our $S^{\theta\theta}$ and his $S^{\theta\theta}$ differ only by a constant. We find that the traction on one of the curved surfaces and on straight edges must also be applied in addition to the couple on the straight edges of the plate whose moment is $-\frac{1}{2} \log (b/a)$.

6. By using the strain energy function, Ericksen[4] has deduced the results similar to those given in (4.25). In hypo-elasticity, where we take rate of stress as a function or rate of deformation, the stresses are obtained without the introduction of a strain-energy function.

In the end, I must thank Prof. B. R. Seth for his helpful guidance in preparation of this work.

Summary

In hypo-elasticity, where we take rate of stress as a function of rate of deformation, *i.e.*, stress increment as a function of small strain from the immediately preceding state, the problems are solved without assuming the stress-strain relations. Here we have shown that in the case of bending a rectangular plate into circular form, the stresses obtained without assuming stress-strain relations are the same as those obtained by Seth[3] after assuming the stress-strain relations.

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STUDIES WITH SCINTILLATION COINCIDENCE SPECTROMETER: Cs^{134}

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Abstract

The set-up of 'Slow-Fast' conicidence scintillation spectrometer is described. Gamma-gamma coincidences in Cs^{134} have been studied. The 604-kev. gamma transition is found to be in cascade with 460 ± 20. 555 ± 15, 794 ± 15 and 1349 ± 30 kev. gamma transitions. The 794-kev. gamma transition is found to be in cascade with 604 ± 10 and 555 ± 15 kev. gamma transitions. The results are consistent with the decay scheme of Cs^{134} proposed by Forster *et al.*[11]

Introduction

Coincidence studies with scintillation counters have been found to be a very useful method of determining the sequence of energy levels in a nucleus formed in a complex beta-decay of a radio-active nucleus. For this purpose a 'slow-fast' coincidence spectrometer as described below has been set up. This instrument was used to investigate the gamma transitions in Ba^{134}, resulting from the complex beta-decay of Cs^{134}. This isotope has been studied by several workers[1–11] and in particular, the gamma-ray energies were determined from the photo-electron spectrum taken in the Siegbahn-Slatis beta-ray spectrometer[7] at this Institute. In the decay of Cs^{134}, eleven gamma transitions of the following energies were reported—467, 553, 571, 607, 794, 1027, 1164, 1368 and 1401 kev. Of these the two gamma-rays at 604 kev. and 794 kev. are the most intense ones. The aim of this work was to determine which of the other gamma transitions are in cascade with these two well-known gamma-rays in Ba^{134}.

In a previous report on beta-gamma and gamma-gamma coincidence study of this isotope, G. Bertollini *et al.*[10], employed discriminators, one in each channel, for energy discrimination, the resolving time of the coincidence unit being $0{\cdot}5\,\mu$ sec. In this work, gamma-gamma coincidences have been studied, employing a shorter resolving time, $1{\cdot}5 \times 10^{-8}$ sec. of the coincidence unit and single channel pulse analysers, one in each channel, for energy selection. This helps in deciding more definitely the energies of gamma-rays that are in cascade and throws some light on the question

of the sequence of levels in Ba^{134}. In particular, as a result of this investigation, it can be argued that the first excited state in Ba^{134} is 604 kev. rather than 794 kev.

Experimental Arrangement

The block diagram of the conventional 'slow-fast' coincidence scintillation spectrometer is shown in Fig. 1. For gamma-gamma coincidence measurements two NaI (TI) crystals each 1″ in diameter and 1″ thick, viewed by two EMI 6260 photomultipliers have been used. Both the crystals were shielded with ½″ thick lead collimators. They were kept 120° apart so that they do not see each other thus minimizing the false coincidences arising from scattering of gamma rays from one crystal to the other.

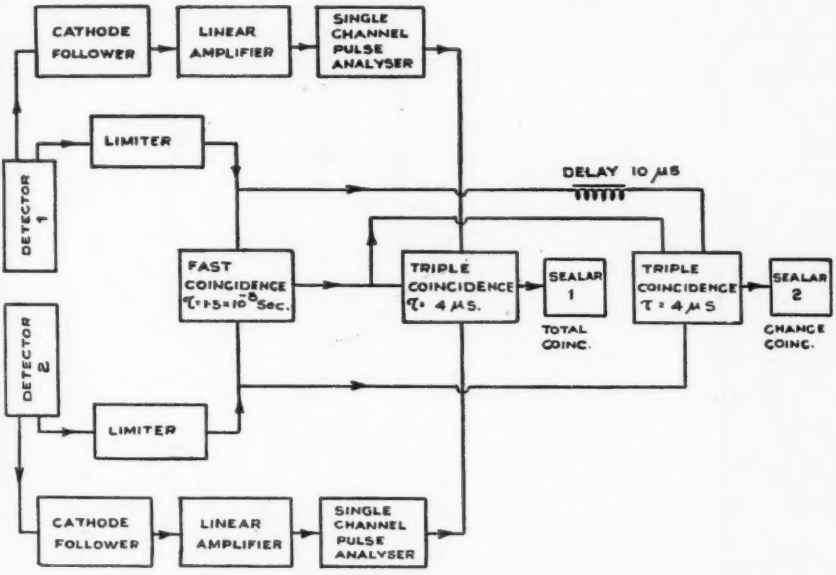

Fig. 1. Block Diagram of Slow-Fast Coincidence Scintillation Spectrometer.

Pulses from the anode of the photomultiplier are limited to an amplitude of ½ volt by a limiter circuit. The limiter output pulses are carried to the fast coincidence unit by a coaxial cable RG8U which is terminated at both ends by its characteristic impedance to eliminate any reflections. These pulses are shaped at the input to the coincidence circuit by 400 cm. long RG8U coaxial cable shorted at the other end. The fast coincidence circuit is a bridge type circuit using crystal diodes. By inserting known delays in

either channel the prompt coincidence due to Co^{60} gammas were counted and from the curve thus obtained, the resolving time of the coincidence unit was determined to be $1{\cdot}5\times10^{-8}$ sec.

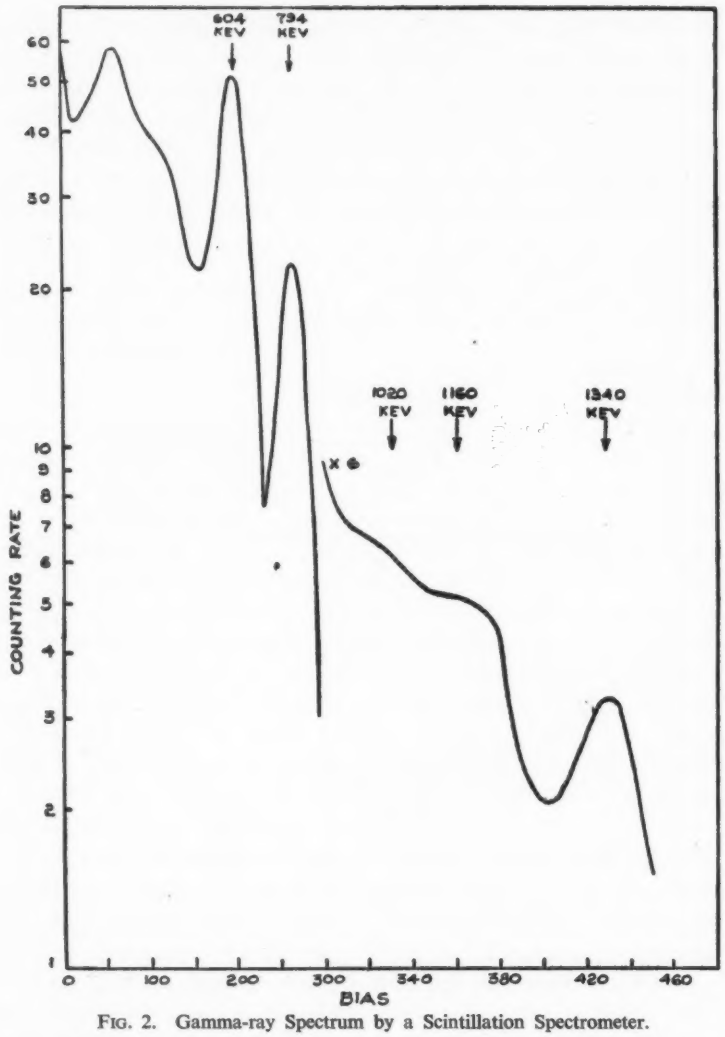

FIG. 2. Gamma-ray Spectrum by a Scintillation Spectrometer.

Pulses from the third dynode, after amplification, are fed to a single channel analyser for energy selection. The fast coincidence output and those

from the two single channel analysers are fed to a slow triple coincidence unit (resolving time 4 μs.) thus enabling coincidences between any two selected energies of gamma-rays to be counted. This indirect method of introducing energy selection to coincidence circuits is necessary, because the fast coincidence unit must be operated by the pulse derived from the first few photo-electrons produced in the photomultiplier, whereas the analyser is required to be triggered by a pulse proportional to the total number of photo-electrons released by the light scintillation from the phosphor. The analyser output pulse will therefore be considerably delayed with respect to the pulse operating the fast coincidence unit and, moreover, this delay will vary with pulse amplitude. The fast coincidence circuit therefore cannot follow the analyser. The chance coincidences are also counted simultaneously by feeding the same three pulses to another triple coincidence unit (resolving time 4 μs.) with one channel delayed by 10 μs.

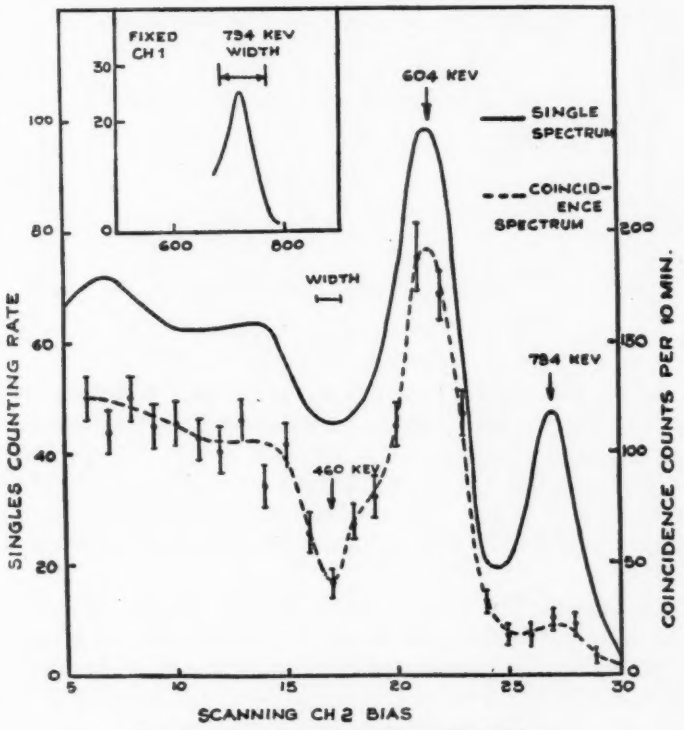

FIG. 3. Spectrum in Coincidence with 794 kev.

RESULTS

Gamma-ray spectra in coincidence with 604 kev., 794 kev. and 1349 kev. respectively were taken. A very strong source was used. The following results are obtained as shown in Figs. 3, 4 and 5:—

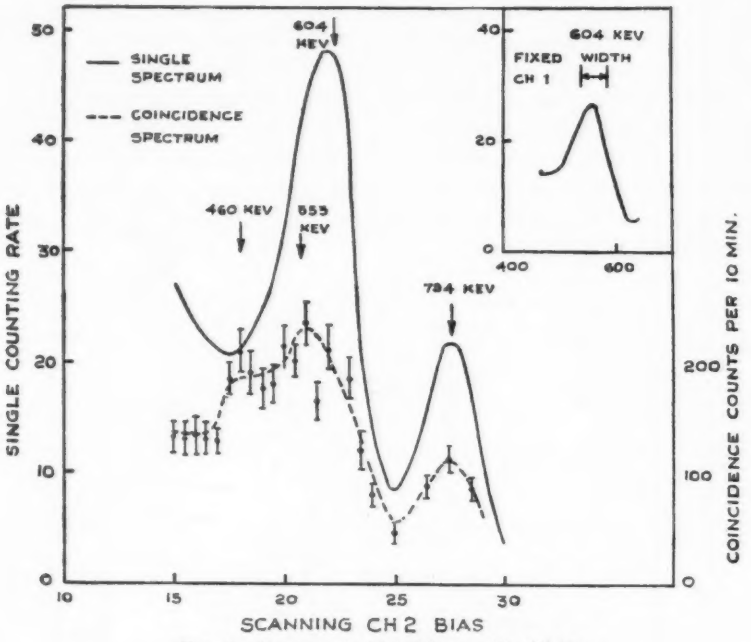

FIG. 4. Spectrum in Coincidence with 604 kev.

1. One channel was fixed to allow full photo-peak of 794 kev. as shown in the inset of Fig. 3. Both crystals were shielded with lead and were kept 120° apart and were arranged to be 2″ from the source. The gamma transitions in coincidence with the 794 kev. gamma-ray are found to be of energies 604 ± 10 and 555 ± 15 kev. There is also strong evidence for the existence of a gamma-ray of energy 460 ± 20 kev., which is not in coincidence with 794 kev. (Fig. 3).

2. One channel was fixed to allow a small fraction of the 604 kev. photo-peak as shown in the inset of Fig. 4. In this case the geometry was the same as above. The gamma-rays in coincidence with 604 kev. gamma-ray are found to be of energies 460 ± 20 kev., 555 ± 15 kev. and 794 ± 15 kev.

3. Finally, one channel was fixed to allow the full photo-peak of 1349 kev. gamma-ray. Since this is weak, the crystal corresponding to this

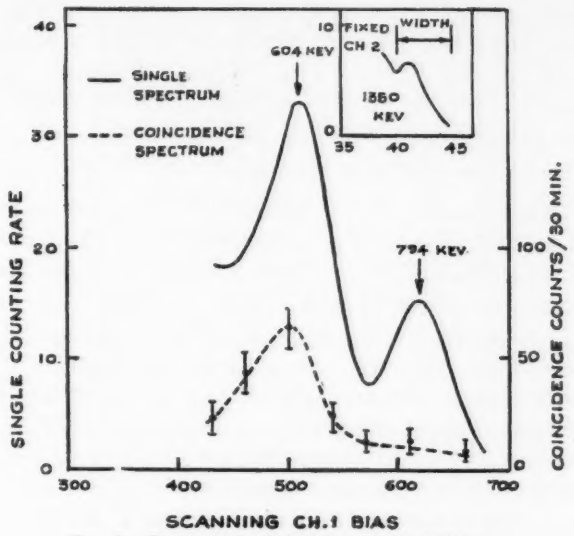

FIG. 5. Spectrum in Coincidence with 1350 kev.

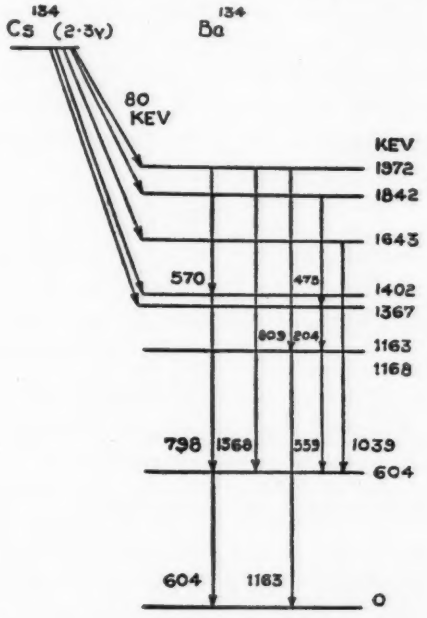

FIG. 6. Decay-Scheme of Cs^{134} Proposed by Forster and Wiggins.

channel was unshielded and kept at a distance of 1·5 cm. from the source. A lead plate, 1 cm. thick, was interposed between this crystal and the source in order to reduce the 604 kev. and 794 kev. radiations. The 1349 kev. gamma-ray is found to be in coincidence with 604 kev. gamma-ray but not with 794 kev. gamma-ray as seen from Fig. 5.

DISCUSSION

All the results obtained in this work, namely, the triple cascade 604 kev.–794 kev.–555 kev. and the double cascades 460 kev.–604 kev. and 1349 kev.–604 kev., are consistent with the decay-scheme of Cs^{134} shown in Fig. 6 which is the decay-scheme proposed by Forster and Wiggins.[11]

The main disagreement between the different decay-schemes proposed for Cs^{134} seems to be about the energy of the first excited state in Ba^{134}. Since the weak gamma 1349 kev. (1369 kev. of Forster[11]) is in cascade with the intense 604 kev. gamma-ray, 604 kev. as the energy of the first excited state seems to be more justified than 794 kev. If 794 kev. is assumed to be the energy of the first excited state, then the 1349 kev. gamma transition has to be to the ground state and the 604 kev. gamma-ray has to be emitted by the highest level 1972 kev. so as to be in cascade with the 1349 kev. transition. In that case, the 604 kev. gamma transition would be a weak one since the 1972 kev. level is formed by a rather weak beta-ray group (80 kev., 28%[11]). In fact 604 kev. gamma-ray has been found to be the most intense one. Hence it is preferable to assume 604 kev. as the energy of the first excited state.

Author's thanks are due to Dr. B. V. Thosar for his interest and helpful suggestions and to Dr. S. Jha for discussion.

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FARADAY ROTATION IN CALCITE

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1. Introduction

As the presence of birefringence in a solid interferes with the measurement of its magneto-optic rotation to a considerable degree, the determination of the Faraday rotation in a highly anisotropic crystal, even along the optic axis presents some experimental difficulty. In spite of its high birefringence, it was in calcite that Chauvin[1,2] verified the laws of propagation of light in a birefringent magneto-optic medium. His choice of this substance was obviously governed by the fact that perfect specimens of this crystal are easily available. Chauvin's researches have demonstrated that the practical difficulties encountered in this field of experimentation are by no means insurmountable.

The magneto-optic rotation of calcite, apart from the problem it presents in its measurement, is interesting in many other respects. Previous researches from this laboratory on the magneto-optic properties of diamond,[3] the alums and sodium chlorate[4] have indicated that the presence of strong covalent bonds in the structure has a tendency to decrease the magneto-optic anomaly factor. Calcite with its CO_3 groups would, therefore, be an ideal substance to investigate. The present paper reports the values of the Faraday rotation in calcite parallel to the optic axis and also records the values of the Verdet constant of sodium chlorate. These measurements have proved quite fruitful in that it has been possible to establish, as had been foreseen by Darwin and Watson[5] (1927) that the magneto-optic anomaly factor for various frequencies responsible for refractive dispersion may be different.

2. The Verdet Constant in Calcite

In a very good rhomb of calcite two faces were cut and polished perpendicular to the optic axis. Great care was exercised (by a series of observations under a polarisation microscope followed by grinding and polishing of the faces) to get the optic axis eaxctly normal to these planes. The softness of the crystal, and the large variety of excellent abrasive and polishing papers that are available in the market to-day, considerably facilitated this process. The crystal was then fixed to a brass gadget (Chauvin[2]) which was capable of delicately rotating it through small angles about two perpendi-

cular axes. With this arrangement the crystal was set between the poles of the electromagnet so that light from a mercury arc passed exactly along the optic axis. The divergence of the light was reduced by first rendering it parallel and then allowing it to pass through four apertures, 3 mm. in diameter, placed at intervals of 50 cm. on either side of the calcite crystal.

Measurement of the rotation was made for λ 5461 with a sugar half shade (Rayleigh[6]), first placed at the polariser end and later at the analyser end. The magnitudes of the rotation with either arrangement did not differ by more than ½% showing that the birefringence and hence the missetting of the crystal was indeed small (Ramachandran and Ramaseshan[7]). The observations for λ 5893, λ 5780 and λ 5461 were made visually and those for λ 4358 and λ 4047 were made by a spectroscopic technique developed by Landau,[8] details of which have been given in an earlier publication.[4] Table I gives the Verdet constant for calcite for different wavelengths. The specimen of calcite, 8·84 mm. thick, gave a rotation of 4·28° for a field of 16540 Oersteds.

It is estimated that the absolute magnitude of the Verdet constants reported are accurate to 3% to 4%, while the errors in the relative dispersion values are less than 1%.

TABLE I

Magneto-Optic Data for Calcite

$\gamma_1 = \gamma_2 = 0{\cdot}825$, $\gamma_3 = 0{\cdot}20$.

λ	Verdet Constant in min./cm./Oersted		$\bar{\gamma}$
	Exp.	Calc.	
5893	0·0185	0·0184	0·488
5780	0·0193	0·0192	0·488
5461	0·0215	0·0216	0·481
4358	0·0360	0·0355	0·480
4046	0·0418	0·0420	0·467

3. THE MAGNETO-OPTIC ANOMALY FACTOR

From the measured values of the rotation and the known refractive dispersion for the ordinary ray in calcite, the magneto-optic anomaly factor $\bar{\gamma}$ was evaluated from the modified Becquerel formula

$$V = \bar{\gamma} \cdot \frac{e}{2mc^2} \lambda \cdot \frac{dn}{d\lambda} \qquad (1)$$

These values have been entered in column 4 of Table I. One notices that with decrease in wavelength, $\bar{\gamma}$ value gradually decreases from 0·488 to 0·467. As the anomaly factor is a measure of the deviation of the Zeeman splitting of the optical absorption frequency from the normal value, the variation of γ with wavelength can only signify that the anomaly factors associated with the various optical absorption frequencies must be different.

If one assumes that the oscillator strengths (*i.e.*, the transition probabilities) of the different dispersion frequencies are not affected by a magnetic field then if

$$n^2 - 1 = \frac{A_1\lambda^2}{\lambda^2 - \lambda_1^2} + \frac{A_2\lambda^2}{\lambda^2 - \lambda_2^2} \cdots\cdots\cdots \qquad (2)$$

then it follows[5] that

$$V = \frac{1}{n} \frac{e}{2mc^2} \left[\frac{\gamma_1 A_1 \lambda_1^2 \lambda^2}{(\lambda^2 - \lambda_1^2)^2} + \frac{\gamma_2 A_2 \lambda_2^2 \lambda^2}{(\lambda^2 - \lambda_2^2)^2} \cdots\cdot \right] \qquad (3)$$

Here $\gamma_1, \gamma_2, \ldots\ldots$, etc., are the anomaly factors for the absorption wavelengths $\lambda_1, \lambda_2, \ldots\ldots$

In the case of calcite it is known that the refractive dispersion can be expressed by the formula

$$n_\omega^2 - 1 = \frac{0{\cdot}43257\,\lambda^2}{\lambda^2 - (0{\cdot}0500)^2} + \frac{0{\cdot}8293\,\lambda^2}{\lambda^2 - (0{\cdot}1000)^2} + \frac{0{\cdot}4337\,\lambda^2}{\lambda^2 - (0{\cdot}1535)^2} + \frac{0{\cdot}61855\,\lambda^2}{\lambda^2 - (6{\cdot}7)^2}$$

(Ramachandran[9])

The magneto-optic dispersion is found to fit the formula

$$V = \frac{1}{n} \frac{e}{2mc^2} \left[\frac{0{\cdot}0008922\,\lambda^2}{\{\lambda^2 - (0{\cdot}0500)^2\}^2} + \frac{0{\cdot}006842\,\lambda^2}{\{\lambda^2 - (0{\cdot}1000)^2\}^2} + \frac{0{\cdot}002044\,\lambda^2}{\{\lambda^2 - (0{\cdot}1535)^2\}^2} \right]$$

from which $\gamma_1 = \gamma_2 = 0{\cdot}825$ and $\gamma_3 = 0{\cdot}20$. *In these formulæ V is in radians and* λ *in microns*. Column (3) of Table I gives the values of the Verdet constant calculated using these values of the magneto-optic anomaly factors.

The agreement between the experimental and calculated values is quite satisfactory.

It is perhaps worthwhile at this stage to emphasise that the determination of γ_1, γ_2, etc., is actually by a " fitting up " process. Therefore values of the anomaly factor of any accuracy or significance can be obtained only if one has (*a*) an accurate dispersion formula for refractive dispersion, using preferably experimentally observed absorption frequencies and also (*b*) very accurate values of the magneto-optic rotation over a wide range of wavelengths. In the case of calcite none of these conditions is very well satisfied. Even so, one notices that the anomaly factor for the absorption wavelength λ 1535, which one could associate with the CO_3 group, is much less than that for the other wavelengths.

4. FARADAY ROTATION IN $NaClO_3$

In view of this significant result it was considered worthwhile to redetermine the magneto-optic constants of $NaClO_3$ which also contains a group having strong covalent bonds. When the measurements were made it was found that the values reported by Voigt[10] and later by Ramaseshan[4] contained a serious numerical error. The reported values were too small by a factor of two. Table II gives the Verdet constants for $NaClO_3$.

TABLE II

Magneto-Optic Data for $NaClO_3$

$\gamma_1 = 0{\cdot}74$ $\gamma_2 = 0{\cdot}46$.

λ	Verdet Constant in min./cm./Oersted		γ
	Exp.	Calc.	
5780	0·0179	0·0179	0·668
5461	0 0203	0·0203	0·669
4358	0·0334	0·0334	0·663
4047	0·0397	0·0397	0 660
3650	0·0508	0·0507	0·653

In this case

$$n^2 - 1 = \frac{1{\cdot}1825\,\lambda^2}{\lambda^2 - (0{\cdot}0900)^2} + \frac{0{\cdot}07992\,\lambda^2}{\lambda^2 - (0{\cdot}1850)^2} - 0{\cdot}00864\,\lambda^2$$

(Chandrasekhar[11])

and

$$V = \frac{1}{n}\frac{e}{2mc^2}\left[\frac{0{\cdot}007088\,\lambda^2}{\{\lambda^2-(0{\cdot}0900)^2\}^2}+\frac{0{\cdot}001258\,\lambda^2}{\{\lambda^2-(0{\cdot}1850)^2\}^2}\right]$$

from which $\gamma_1 = 0{\cdot}74$ and $\gamma_2 = 0{\cdot}46$.

The calculated values using these constants have been entered in column (3) while column (4) gives the values of the mean anomaly factor using formula (1).

Here again one notices that the γ values for an absorption wavelength associated with a covalent group (λ 1850) is much lower than that for other wavelengths. It is, therefore, worthwhile to undertake the accurate measurement of the magneto-optic rotation, over a wide range of wavelengths for a large number of crystals. For such measurements a sensitive photo-electric polarimeter for visible and ultraviolet work has been developed by one of the authors (V.S.) and the results of the studies using it will be reported in due course.

5. Summary

The Faraday rotation has been measured in calcite parallel to the optic axis for the wavelengths λ 5893, λ 5780, λ 5461, λ 4358 and λ 4047 Å. A dispersion formula for the magnetic rotation has been fitted up using the same absorption frequencies that are used in refractive dispersion. It is shown that the magneto-optic anomaly factors for the various absorption frequencies are different and the value of the anomaly factor for the absorption wavelength λ 1535, is very much lower than that for the other absorption wavelengths. ($\gamma_{1575} = 0{\cdot}20$, $\gamma_{1000} = \gamma_{500} = 0{\cdot}825$.) This paper also reports the values of the Verdet constant of $NaClO_3$ for a few wavelengths from λ 5780 to λ 3650 Å. A numerical error in the earlier measurements has been noticed and rectified here. In this case also a dispersion formula for magnetic rotation has been proposed and it is found that for this crystal $\gamma_{1850} = 0{\cdot}46$ while $\gamma_{900} = 0{\cdot}74$.

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DISPERSION OF FARADAY ROTATION IN FUSED QUARTZ

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1. Introduction

Although crystalline quartz has been the subject of many investigations, very few accurate studies have been made on the magnetic and optical properties of fused quartz. The dispersion of magnetic gyration in crystalline quartz has been measured by Borel (1903), Disch (1903), Lowry (1912) and Ingersoll (1917) over a wide range of wavelengths. But for fused quartz the Verdet constant has been determined for only three wavelengths λ 5893, λ 5461 and λ 4358 Å (Stierlin, 1907; Lowry, 1912; Cotton, 1931; and Ramaseshan, 1946) and even here there seems to be considerable disagreement in the values reported. The refractive indices and the elastic constants of this substance also show variation from specimen to specimen. Till recently, most of the specimens of fused silica that were available, showed a curious strain structure probably caused by the structural birefringence arising from the previous thermal and mechanical history of the specimen (Raman, 1950). These flaws in the internal constitution of the specimens were obviously the cause for the discrepancies found in the measurements of the many physical properties of the substance.

The Thermal Syndicate Ltd., London, has now been able to produce large specimens of very high optical quality fused quartz. A specimen of size $1'' \times 1'' \times 2''$ acquired by Prof. R. S. Krishnan from this concern for the study of light scattering and Raman effect was used in the present investigation. This specimen was found to be perfectly homogeneous and free from any inclusions, exhibiting a beautiful bluish track when a beam of light passed through it. Using this specimen, the absolute values of magnetic rotations for fused quartz have been determined accurately for different wavelengths from λ 5780 to λ 2848 Å, and the results have been compared with those of crystalline quartz. The dispersion of magnetic gyration has also been correlated to the optical dispersion and the validity of the modified Becquerel formula has been tested.

2. Experimental Technique

The magnet used in these experiments was of the Rutherford type fitted with special pole-pieces. Both visual and photoelectric techniques were em-

ployed for the determination of the magnetic rotations. A Lippich double field polariser and an analyser mounted on a divided circle that could read up to 0·01°, were used in the visual measurements. The complete experimental set-up and procedure for visual measurements have already been given in an earlier publication (Sivaramakrishnan, 1954).

In the experimental set-up for the photoelectric method, the Lippich half-shade polariser was replaced by an ultraviolet nicol. The light from the analyser was focussed on to the slit of a monochromator capable of covering the whole wavelength range in the visible and the ultraviolet. A R.C.A. 1.P. 28 type photomultiplier tube was housed in a light-tight box attached to the exit slit of the monochromator. The power supply of 1000 V.D.C. for the photomultiplier tube was well smoothed and regulated. The complete wiring diagram of the photomultiplier with the power supply is given in Fig. 1. The output from the photomultiplier tube was either fed to a galvanometer directly or to a cathode-ray oscillograph through an A.C. amplifier. In the direct current measurement method, the dark current of the photomultiplier tube which is of the order of 10^{-8} amps. was compensated by a counter electromotive force from a battery. This method was not however extremely satisfactory when very great accuracy was aimed at, as the dark current was not constant but fluctuated erratically.

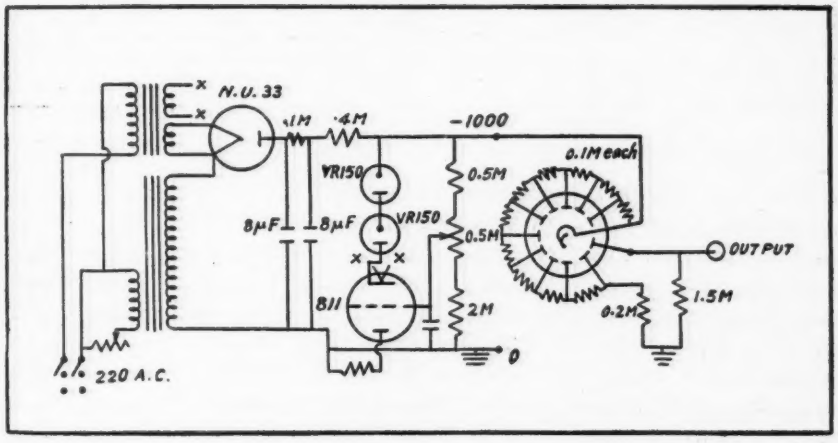

FIG. 1. Photomultiplier circuit diagram.

Therefore for most of the measurements, only the A.C. method of detection was adopted. For this the incident light was modulated by running

the high pressure mercury discharge lamp source on the 50 cycles mains. The source was fairly stable in intensity as it had an intensity stabilizer unit. The signal from the photomultiplier was fed to a cathode-ray oscillograph through a narrow band amplifier. As in an A.C. amplifier the noise is proportional to the band width, the narrowing of the band width would considerably reduce the thermal noise from the phototubes, the hum from the power supply and the external sources which might arise due to imperfect shielding, etc. The amplifier used is similar to the one described by Miller, Long, Woodward and Thompson (1949) and Suryan (1953), but modified to suit the present investigation. The circuit diagram is given in Fig. 2. The

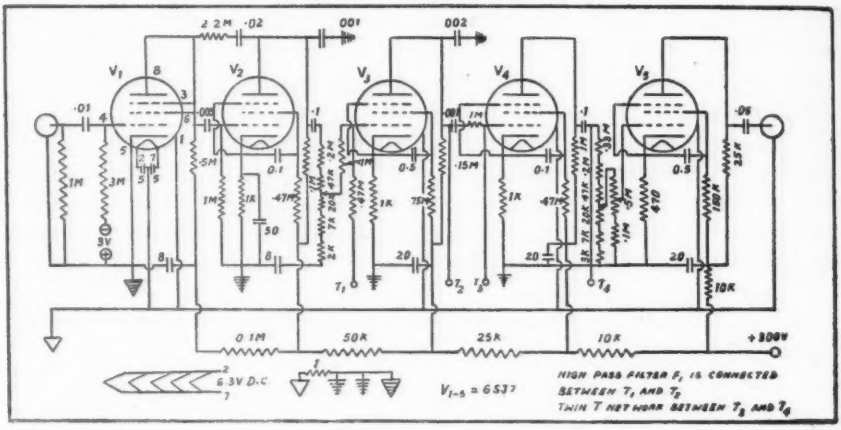

FIG. 2. Narrow band amplifier.

amplifier was adjusted for maximum response at 100 cycles by the two filters F_1 and F_2 which were high pass and Twin-T network filters respectively. The amplification was controlled by means of three variable controls and extensive screening was done in the earlier stages to avoid the interference and spurious pick-ups. The sensitivity of detection could be increased further by using a phase detector with the narrow band amplifier. With such an arrangement, it would have been possible to detect rotations to a few seconds of an arc. However, various other factors limiting the accuracy of measurement, such as the stability of the magnetic field, the stability of the light intensity, and the maximum precision with which the analyser readings could be read, did not warrant the use of this more sensitive device. It was found possible, to measure the rotations accurately to ·01° with the present set-up itself.

"The method of total extinction" and "the method of symmetrical angles" (Heller) were used for the measurement of rotations. With the same set-up it was possible to adopt both the methods. The experimental procedure is as follows. The substance under study was placed in between the pole-pieces of the magnet, and the two nicols were set for the total extinction position. The analyser reading θ was noted. Later the magnetic field was put on and the analyser rotated so that there was minimum output from the photomultiplier tube as shown by the height of the peak of the 100 cycles sine wave in the cathode-ray oscillograph. Then the analyser reading θ_2 was noted and $(\theta_2 - \theta_1)$ gave the approximate magnetic rotation for the substance for that particular field. Later the analyser was rotated and set at two positions A_1 and A_2 at which the output from the photomultiplier was equal, on either side of the approximate extinction position θ_1. The mean of the two settings, *i.e.*, $(A_1 + A_2)/2$, gave the exact position of extinction. The rotations were measured with the magnetic field on and reversed. Usually the gain of the amplifier was altered by means of the attenuators and the rotations were determined at various amplifications. Also several readings were taken to avoid the errors due to fatigue effects. Measurements were made at number of wavelengths from λ 5780 to λ 2848 Å and the rotations were found to be accurate to ·01°.

When solids with residual birefringence are placed in between the polariser and the analyser, it is not possible to set the two for toal extinction. This is overcome by compensating the signal from the photomultiplier tube (arising from the residual light intensity at the crossing position), by means of another signal from a second photomultiplier tube facing the same source of light. The two signals are mixed in a difference amplifier which precedes the main narrow band amplifier.

The magnetic field was determined by measuring the rotation produced by conductivity water of known thickness (approximately the same thickness as the specimen). The Verdet constant for water at λ 5461Å at 25° was taken to be ·01547 minutes/cm./Oersted. (Rodger and Watson.)

3. Experimental Results

The Verdet constant has been determined with light travelling perpendicular to all the three pairs of faces of the fused quartz block and it was found to be constant within $\frac{1}{2}$%. The specimen was also rotated about an horizontal axis parallel to the direction of propagation of light and again the Verdet constant was practically constant with no systematic variation, thereby revealing the absence of any perceptible birefringence in the specimen.

(Ramachandran and Ramaseshan, 1952). The average value of the Verdet constant has been taken for the fitting up of a dispersion formula.

In Table I are given the experimental values of the Verdet constant for different wavelengths.

TABLE I

Magneto-Optical Data for Fused Quartz

Wavelength Å	Refractive Index	Verdet Constant min./cm./Oersted		γ	Mean value of γ
		Calc.	Exp.		
5780	1·4589	0·01538	0·01540	0·794	
5461	1·4601	0·01733	0·01731	0·792	
4916	1·4628	0·02173	0·02183	0·796	
4358	1·4667	0·02828	0·02837	0·796	
4047	1·4697	0·03337	0·03349	0·796	0·793
3650	1·4744	0·04214	0·04224	0·796	
3342	1·4800	0·0518	0·0516	0·790	
3132	1·4845	0·06061	0·06059	0·793	
3022	1·4869	0·06614	0·06600	0·792	
2967	1·4887	0·06932	0·0690	0·790	
2848	1·4931	0·0768	0·0763	0·789	

It is worthwhile to compare the values of Verdet constant found in the present studies with those of Cotton (1931) and Ramaseshan (1946). The values of Verdet constant for the wavelengths λ 5780, λ 5461 and λ 4358 of the above workers are given in Table II along with the values of the author.

TABLE II

Wavelength Å	Verdet constant min./cm./Oersted		
	Cotton	Ramaseshan	Author
5780	0·01479	0·01491	0·01540
5461	0·01671	0·01664	0·01731
4358	0·02602	0·02640	0·02837

It can be noticed that the values of Ramaseshan and Cotton differ from the author's values by 4% at λ 5461 and by 8% at λ 4358 Å. This may prob-

ably be due to the slight birefringence in the specimens studied by them. When birefringence is present, the observed rotations would be less than the actual ones, and the magnitude of the difference between the apparent and the actual rotations would increase with the decrease in wavelength (Sivaramakrishnan and Ramaseshan, 1956). This is found to be true in the present case thus supporting the idea of the presence of residual birefringence in the specimens studied by previous authors.

For evaluating the value of the anomaly factor we shall consider the dispersion formula proposed by Chandrasekhar (1951),

$$n^2 - 1 = \frac{0{\cdot}5320\,\lambda^2}{\lambda^2-(0{\cdot}0600)^2} + \frac{0{\cdot}4151\,\lambda^2}{\lambda^2-(0{\cdot}1060)^2} + \frac{0{\cdot}1570\,\lambda^2}{\lambda^2-(\cdot 1190)^2} + \frac{0{\cdot}4538\,\lambda^2}{\lambda^2-(8{\cdot}84)^2} + \frac{1{\cdot}4460\,\lambda^2}{\lambda^2-(20{\cdot}74)^2}$$

which is found to fit the experimental data on refractive indices very satisfactorily.

By using the modified Becquerel formula, $V = \bar{\gamma}\frac{e}{2mc^2}\lambda\frac{dn}{d\lambda}$, where V is the Verdet constant, γ the weighted mean value of the anomaly factor of the different absorption frequencies, the value of $\bar{\gamma}$ was evaluated at various wavelengths from the experimental values of Verdet constant and the total dispersion $dn/d\lambda$ obtained from the above formula for refraction. The evaluated values of $\bar{\gamma}$ are given in Table I, Column 5. It can be noticed that the value of $\bar{\gamma}$ for this substance in the wavelength region studied is practically constant, the variation being less than 1%. This clearly indicates that all the absorption frequencies that are responsible to refractive dispersion, are effective towards dispersion of magneto-optic rotation in the same proportion as in refraction.

Therefore the following dispersion formula for magnetic gyration using all the absorption frequencies that are responsible towards refraction is proposed.

$$V = \frac{e}{2mc^2}\frac{1}{n} \times 0{\cdot}793 \left\{ \frac{0{\cdot}001915\,\lambda^2}{\left(\lambda^2-(0{\cdot}0600)^2\right)^2} + \frac{\cdot 004664\,\lambda^2}{\left(\lambda^2-(0{\cdot}1060)^2\right)^2} + \frac{\cdot 002223\,\lambda^2}{\left(\lambda^2-(0{\cdot}1190)^2\right)^2} \right\}$$

Here V is in radians and λ is in microns.

The contribution to magnetic rotation by the infra-red frequencies is negligible and is not therefore taken into consideration. The value of the

mean anomaly factor for fused quartz is 0·793. The Verdet constant for various wavelengths were calculated from the above formula, and are given in Table I. The calculated and the experimental values agree fairly well to ½%, which is the order of the experimental accuracy.

4. MAGNETO-OPTIC ROTATION IN CRYSTALLINE AND FUSED QUARTZ

As is well known, the formation of fused quartz from crystalline quartz when the latter is melted, is accompanied by a considerable diminution in the density from 2·651 to 2·203 and also diminution of the coefficient of thermal expansion which is 36×10^{-6} for quartz and only $1{\cdot}5 \times 10^{-6}$ for vitreous silica. We shall consider here the Faraday rotation and the optical refraction in these cases. The additive constant in the case of refractive index is refractivity and is given by

$$\frac{n^2-1}{n^2+2}\frac{1}{d} \text{ or } \frac{n^2-1}{d}$$

depending on whether the Lorentz-Lorenz polarisation field is present inside the crystal or not. Similarly the additive constants for magnetic rotation is magnetic rotativity defined as

$$\frac{9n}{(n^2+2)^2}\frac{V}{d} \text{ or } \frac{nV}{d}.$$

The significance of rotativity is that for a substance it remains constant even when the density changes. Table III gives the optical and the magneto-optical constants for crystalline and fused quartz.

TABLE III

Substance	Density	Refractive index 5780	λ 5780 Verdet Constant min./cm./ Oersted	Refractivity		Rotativity	
				$\frac{n^2-1}{d}$	$\frac{n^2-1}{n^2+2}\frac{1}{d}$	$\frac{nV}{d}$	$\frac{9n}{(n^2+2)^2}\frac{V}{d}$
Crystalline quartz	2·651	1·5447	·01714	0·5228	0·1191	·00999	·00467
Fused quartz ··	2·208	1·4590	·01540	0·5111	0·1238	·01017	·00537

It can be noticed from the table that both the Verdet constant and the refractive index for fused silica are significantly lower than the corresponding constants for crystalline quartz. Also it can be seen that while there is a variation of only 2% in the values of nV/d for these substances, the variation in $\frac{9n}{(n^2+2)^2}\frac{V}{d}$ is more than 10%. This is rather disturbing as these

results seem to throw a serious doubt on the very existence of Lorentz-Lorenz polarisation field in quartz. On the other hand this may also signify that fused quartz is fundamentally different in structure from crystalline quartz.

We shall now consider the calculated values of anomaly factor for quartz from the values of Verdet constant reported by Borel. The optical dispersion $dn/d\lambda$ was determined from the dispersion formula proposed by Radhakrishnan (1951), who makes use of the same absorption frequencies that are used in the refractive dispersion formula of fused quartz. Table IV gives Borel's values of Verdet constant for crystalline quartz and the calculated value of $\bar{\gamma}$ for various wavelengths.

TABLE IV

Magneto-Optical Data for Crystalline Quartz

Wavelength Å	Refractive Index	Verdet Constant min./cm./Oersted	$\bar{\gamma}$
6438	1·5423	0·01368	0·773
5893	1·5443	0·01664	0·777
5466	1·5462	0·01952	0·778
5086	1·5482	0·02257	0·773
4799	1·5501	0·02574	0·778
4678	1·5516	0·02750	0·785
4358	1·5538	0·03181	0·779
3612	1·5635	0·04617	0·740
2573	1·5962	0·1079	0·747

It can be seen from the table that the value of $\bar{\gamma}$ drops down suddenly after λ 4358 Å, for the two wavelengths for which measurements have been made. More extensive measurements in the ultraviolet region are needed before his data could be accepted as showing a real variation in $\bar{\gamma}$ with wavelength. But if one considers only the values of Verdet constant from λ 6438 Å to λ 4358 Å, the following dispersion formula fits the experimental data on magnetic gyration fairly well.

$$V = \frac{e}{2mc^2}\frac{1}{n} \times 0{\cdot}776 \left\{ \frac{0{\cdot}002387\,\lambda^2}{\left(\lambda^2 - (0{\cdot}0600)^2\right)^2} + \frac{0{\cdot}005819\,\lambda^2}{\left(\lambda^2 - (0{\cdot}1060)^2\right)^2} + \frac{0{\cdot}002491\,\lambda^2}{\left(\lambda^2 - (0{\cdot}1190)^2\right)^2} \right\}.$$

The value of the anomaly factor $\bar{\gamma}$ is 0·776.

It is most interesting to note here that while the values of the Verdet constant of fused quartz is less than that of crystalline quartz, the anomaly factor $\bar{\gamma}$ in the former is slightly greater than that in the latter.

5. SUMMARY

The complete experimental set-up of an accurate photoelectric polarimeter with an ultraviolet sensitive photomultiplier, a tuned amplifier followed by a cathode-ray oscillograph has been described in this paper. This has been used for the measurement of Faraday rotation in a perfect fused quartz specimen showing no residual birefringence. Measurements have been made for number of wavelengths λ 5780 to λ 2848 Å. The following dispersion formula for magneto-optic rotation which fits the experimental data to ½% has been proposed using the same absorption frequencies that are responsible for refractive dispersion,

$$V = \frac{e}{2mc^2}\frac{1}{n} \times 0{\cdot}793 \left[\frac{0{\cdot}001915\,\lambda^2}{\left(\lambda^2 - (0{\cdot}0600)^2\right)^2} + \frac{0{\cdot}004664\,\lambda^2}{\left(\lambda^2 - (0{\cdot}1060)^2\right)^2} + \frac{0{\cdot}002223\,\lambda^2}{\left(\lambda^2 - (0{\cdot}1190)^2\right)^2} \right]$$

where V is in radians and λ in microns.

The magneto-optic anomaly factor is 0·793 for all the absorption frequencies. The available data on crystalline quartz has also been analysed and the values of the Verdet constant, the magneto-optic anomaly factor and the magnetic rotativity of the two substances have been compared and found to be significantly different.

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MAGNETO-OPTIC STUDIES IN THE NITRATES OF LEAD, BARIUM AND STRONTIUM

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1. Introduction

Measurements of the Faraday rotation in calcite and sodium chlorate have revealed that the magneto-optic anomaly factors for the different absorption frequencies of a substance may be different. It is also found that the anomaly factors for the frequencies which correspond to the anisotropic groups like CO_3, ClO_3, etc., are very low (Ramaseshan and Sivaramakrishnan, 1956). This idea has been supported by the studies of the author (1954) on ionic solutions where he found that the solvated nitrate ion had an extremely low value of 0·08 for the anomaly factor. The study of the magneto-optic properties of solids with nitrate groups in them would therefore prove to be of great interest. The nitrates of lead, barium and strontium which were known to crystallise in the cubic system and could be quite easily obtained from aqueous solutions, were therefore chosen for the investigation reported in this paper. No measurements of the Faraday rotation in these crystals have so far been made. This is probably because of the fairly high residual birefringence that these crystals exhibit. The method recently developed by Sivaramakrishnan and Ramaseshan (1956) has been employed here for eliminating the effects of accidental birefringence in these crystals. The Verdet constant has been determined accurately for a number of wavelengths from λ 5780 to λ 3650 Å using the photoelectric polarimetry technique. The values of the magneto-optic anomaly factor have been evaluated using the refractive dispersion values of Poinsot and Mathieu (1955). New dispersion formulæ for both optical refraction and magnetic gyration have been proposed here.

2. Materials and Methods

The crystals of barium and strontium nitrates were grown in this laboratory by Dr. K. Vedam from warm-saturated solutions of the salts. Since the crystals were grown above 25° C., they were free from any water of hydration. The specimens were 4 to 5 mm. in thickness and 2 sq. cm. in area and were found to be slightly birefringent. The crystal of lead nitrate used was

from Professor Krishnan's collection and its size was $1 \cdot 5 \times 1 \times 1$ cm. All these crystals exhibited a preferred axis of strain.

The magneto-optic rotation in these crystals has been determined for a number of wavelengths from λ 5780 to λ 3650 Å. The measurements could not be extended below λ 3600 Å, since they were not appreciably transparent below that region. The photoelectric polarimetry method with A.C. compensation (Sivaramakrishnan, 1956) was adopted here for the measurements. The crystal was set such that the incident light vibration was parallel to the principal axis of strain. The apparent rotation ψ_0 was then determined and later the polariser was rotated through 45° and ψ_{45} was determined. From these values the true rotation ρ was evaluated using the formula $3\rho = 2\psi_0 + \psi_{45}$ (Sivaramakrishnan and Ramaseshan, 1956). Since the specimens of $Ba(NO_3)_2$ and $Sr(NO_3)_2$ were less than $0 \cdot 5$ cm. in thickness, the rotations were of the order of 1° to 2° only. Therefore the values of the Verdet constant for these two crystals are accurate to 1% only, while they are accurate to $\frac{1}{2}$% in $Pb(NO_3)_2$. The effective magnetic field was estimated by measuring the rotation produced in conductivity water of the same thickness as the specimens.

3. Dispersion Formulæ for Refraction

The data of Poinsot and Mathieu on the refractive indices of these crystals were used in the fitting up of the dispersion formulæ. Although the formulæ proposed by these authors fit the experimental data on refractive indices well in the visible region of the spectrum, the fit in the ultraviolet region is very unsatisfactory. Therefore, new dispersion formulæ of the Drude type have been proposed using reasonable absorption frequencies.

For the fitting up of a dispersion formula it is necessary to consider the absorption frequencies in the ultraviolet. But unfortunately the ultraviolet absorption frequencies have not been observed so far in these crystals. However, it is known from the absorption spectra studies in aqueous solution of KNO_3, that there is a strong absorption band near about λ 2100 Å. This has been ascribed to the nitrate ion (Maslakowez, 1928). Therefore, one of the absorption wavelengths for these crystals has been taken to be near about λ 2100 Å. Apart from this one, there may be many more absorption frequencies in these crystals. Since we do not know any of these frequencies experimentally, all these unknown frequencies are lumped up into one and dispersion formulæ having only two terms have been proposed here. Moreover, since the data on refraction itself is accurate only to few units in the fourth decimal place, it is not worthwhile to attempt at a formula of many terms.

The dispersion formulæ for refraction proposed now are as follows.

$Pb(NO_3)_2$:—

$$n^2 - 1 = \frac{0{\cdot}5740\,\lambda^2}{\lambda^2 - (0{\cdot}2250)^2} + \frac{1{\cdot}4610\,\lambda^2}{\lambda^2 - (0{\cdot}1048)^2} + \frac{0{\cdot}9262\,\lambda^2}{\lambda^2 - (7{\cdot}143)^2}$$

$Sr(NO_3)_2$:—

$$n^2 - 1 = \frac{0{\cdot}21174\,\lambda^2}{\lambda^2 - (0{\cdot}2250)^2} + \frac{1{\cdot}2417\,\lambda^2}{\lambda^2 - (0{\cdot}1010)^2}$$

$Ba(NO_3)_2$:—

$$n^2 - 1 = \frac{0{\cdot}2172\,\lambda^2}{\lambda^2 - (0{\cdot}2250)^2} + \frac{1{\cdot}768\,\lambda^2}{\lambda^2 - (0{\cdot}0950)^2}$$

It may be noted here that in these formulæ the complete contribution due to the infrared frequencies has not been taken into consideration. This is because of lack of data on refractive dispersion in the infrared and the little contribution made by these frequencies in the visible and the ultraviolet regions of the spectrum. Further we are interested only in the magneto-optic properties of these substances for which the infrared frequencies do not contribute much. However, it must be remembered that in order to satisfy the experimental data on dielectric constant, it is necessary to take them into consideration in the dispersion formulæ.

The absorption wavelength λ 2250 Å which has been used for all the crystals may correspond to that of the nitrate ion. The second absorption wavelength varies with the substance. By using the above dispersion formulæ the refractive indices were calculated for various wavelengths and are given in Table I, along with the experimental ones and the difference between them.

It can be noticed from the table that the experimental and the calculated values agree well to a few units in the fourth decimal place. This is quite satisfactory when compared with the formulæ proposed by Poinsot and Mathieu, where the difference between the calculated and the experimental values occurs in the second place of decimals for some wavelengths.

4. Magneto-Optic Anomaly Factors

As pointed out by Ramaseshan and Sivaramakrishnan (1956), if we assume the refractive dispersion to be represented by a formula

$$n^2 - 1 = \sum_i \frac{A_i \lambda^2}{\lambda^2 - \lambda_i^2}$$

then it follows that

$$V = \frac{1}{n} \frac{e}{2mc^2} \sum_i \frac{\gamma_i A_i \lambda_i^2 \lambda^2}{(\lambda^2 - \lambda_i^2)^2}$$

TABLE I. *Refractive Index Data of the Nitrates*

Wavelength in Å	Lead Nitrate			Strontium Nitrate			Barium Nitrate		
	cal.	exp.	$\Delta n \times 10^4$	cal.	exp.	$\Delta n \times 10^4$	cal.	exp.	$\Delta n \times 10^4$
7682	1·7621	1·7614	+7	1·5796	1·5796	0			
6926	1·7686	1·7683	+3	1·5828	1·5826	+2			
6438	1·7740	1·7745	−5	1·5856	1·5857	−1	1·5653	1·5656	−3
5893	1·7817	1·7820	−3	1·5897	1·5898	−1	1·5692	1·5693	−1
5790	1·7834	1·7833	+1	1·5906	1·5908	−2	1·5701	1·5701	0
5461	1·7896	1·7900	−4	1·5940	1·5940	0	1·5732	1·5732	0
5086	1·7986	1·7983	+3	1·5987	1·5988	−1	1·5777	1·5775	+2
4800	1·8072	1·8069	+3	1·6033	1·6032	+1	1·5821	1·5819	+2
4678	1·8114	1·8114	0	1·6056	1·6057	−1	..	..	..
4358	1·8248	1·8250	−2	1·6127	1·6127	0	1·5911	1·5915	−4
4046	1·8423	1·8417	+6	1·6219	1·6221	−2			
3652	1·8749	1·8747	+2	1·6388	1·6388	0			
3342	1·9157	1·9155	+2	1·6395	1·6594	+1			
3130				1·6805	1·6802	+3			

where γ_is are the anomaly factors for the absorption wavelengths λ_is. If γ_is are the same, then the value of the mean anomaly factor $\bar{\gamma}$ in the modified Becquerel relation

$$V = \bar{\gamma} \frac{e}{2mc^2} \lambda \frac{dn}{d\lambda}$$

would be constant. From the dispersion formula for optical refraction proposed here, the values of $dn/d\lambda$ for various wavelengths were determined for these nitrates and the mean anomaly factors $\bar{\gamma}$ were evaluated. It was found that the value of $\bar{\gamma}$ decreased with the decrease in wavelength. The decrease in the value of $\bar{\gamma}$ was found to be 10% in $Pb(NO_3)_2$ and more than 20% in $Ba(NO_3)_2$ and $Sr(NO_3)_2$ crystals. This clearly indicates that the contributions to magnetic gyration by the two absorption wavelengths are not in the same proportion as in refraction. Therefore dispersion formulæ for magnetic gyration have been constructed with different values of anomaly factor for the two absorption wavelengths that are responsible for refractive dispersion.

The formulæ are as follows:

$Pb(NO_3)_2$:—

$$V = \frac{e}{2mc^2} \frac{1}{n} \left\{ \frac{0{\cdot}01039\,\lambda^2}{(\lambda^2 - (0{\cdot}2250)^2)^2} + \frac{0{\cdot}01367\,\lambda^2}{(\lambda^2 - (0{\cdot}1048)^2)^2} \right\}$$

$Sr(NO_3)_2$:—

$$V = \frac{e}{2mc^2} \frac{1}{n} \left\{ \frac{0{\cdot}000658\,\lambda^2}{(\lambda^2 - (0{\cdot}2250)^2)^2} + \frac{0{\cdot}004979\,\lambda^2}{(\lambda^2 - (0{\cdot}1010)^2)^2} \right\}$$

$Ba(NO_3)_2$:—

$$V = \frac{e}{2mc^2} \frac{1}{n} \left\{ \frac{0{\cdot}000468\,\lambda^2}{(\lambda^2 - (0{\cdot}2250)^2)^2} + \frac{0{\cdot}005417\,\lambda^2}{(\lambda^2 - (0{\cdot}0950)^2)^2} \right\}$$

where V is in radians and λ in microns.

The Verdet constants were calculated from these formulæ for various wavelengths and are given in Table II along with the experimental values of Verdet constant and the evaluated values of mean anomaly factor $\bar{\gamma}$. The values of γ_1 and γ_2 for the three nitrates are as follows:

Substance	γ_1	γ_2
Lead nitrate	0·36	0·85
Strontium nitrate	0·061	0·40
Barium nitrate	0·043	0·51

TABLE II

Magneto-Optic Data for the Nitrates

Substance	Wavelength in Å	Verdet Constant min./cm./Oersted		$\bar{\gamma}$
		cal.	exp.	
$Pb(NO_3)_2$ ..	5780	0·0492	0·0491	0·505
	5461	0·0563	0·0561	0·499
	4916	0·0732	0·0733	0·494
	4358	0·1010	0·1013	0·483
	4047	0·1253	0·1253	0·473
	3650	0·1743	0·1738	0·456
$Sr(NO_3)_2$ ..	5780	0·0125	0·0124	0·222
	5461	0·0133	0·0133	0·216
	4358	0·0223	0·0225	0·202
	4047	0·0267	0·0264	0·189
	3650	0·0348	0·0348	0·177
$Ba(NO_3)_2$ ..	5780	0·0122	0·0123	0·241
	5461	0·0138	0·0137	0·234
	4358	0·0228	0·0229	0·214
	4047	0·0270	0·0270	0·201
	3650	0·0347	0·0346	0·182

It can be easily seen from the table, that the experimental and the calculated values of Verdet constant agree fairly well within the limits of experimental error. It can also be seen that the value of the anomaly factor γ_1, corresponding to the absorption wavelength λ 2250 Å is very much lower than that for the other absorption wavelength in all the three crystals. In $Ba(NO_3)_2$ and $Sr(NO_3)_2$, the values of $\gamma_{(2250)}$ are extremely low and are almost equal. In the studies on the ionic solutions by the author, it has been noticed that the value of the anomaly factor for the nitrate ion at infinite dilution is 0·08 which strongly supports the view that the absoprtion wavelength at λ 2250 corresponds to that of the covalent nitrate ion. But in the case of $Pb(NO_3)_2$, the value of the anomaly factor for the same absorption wavelength λ 2250 Å is higher and is equal to 0·36. This may possibly be due to the existence in the substances containing lead ions, of another absorption frequency near about λ 2000 Å, whose γ factor is very much higher. Studies of the author on the magneto-optic properties of lead glasses seem to lend support to this conjecture.

A critical study of the magnitude of the anomaly factor $\bar{\gamma}$ and γ_2 reveals some interesting features. It can be easily noticed that the value of $\bar{\gamma}$ and γ_2 in barium and strontium nitrates are lower than the corresponding values in the lead salt. This may probably be due to the tighter binding present in barium and strontium nitrates than in lead nitrate. Since a low value of the anomaly factor indicates a partial covalent binding, one could conclude that the binding in barium and strontium nitrates is more covalent than in lead nitrate. This conclusion is supported by other physical constants of these substances (Srinivasan, 1955). It is also supported from studies on Raman effect. The lattice lines appearing in the Raman spectrum of barium nitrate is found to be more intense than those in the lead salt (Couture & Mathieu, 1947).

5. SUMMARY

The Verdet constant has been determined for the nitrates of lead, barium and strontium from λ 5780 to λ 3650 Å. Dispersion formulæ have been constructed for both optical refraction and magneto-optic rotation using the same absorption frequencies in both. In these nitrates it is found that the value of magneto-optic anomaly factor is different for the different absorption wavelengths of the substance and the value of γ for the frequency corresponding to the nitrate ion is extremely low, and is equal to 0·06. The results indicate that the binding in barium and strontium nitrates may be more covalent than that in lead nitrate.

ACKNOWLEDGEMENT

The author thanks Prof. R. S. Krishnan for his kind interest and encouragement, and Dr. S. Ramaseshan for the helpful discussions. He is also grateful to Dr. K. Vedam for supplying the specimens of barium and strontium nitrates grown by him in this laboratory.

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SYNTHESIS OF ANGOLENSIN

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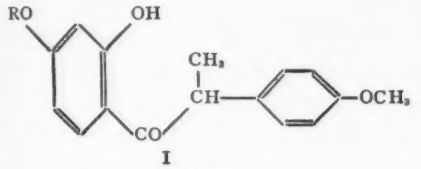
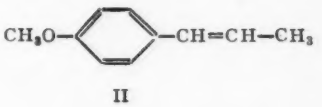
Angolensin (I *a*), an α-methyl-desoxy benzoin related to isoflavones, was first isolated by King, King and Warwick[1] from the wood of *Pterocarpus angolensis* and later by Gupta and Seshadri[2] from the wood and bark of *Pterocarpus indicus*. Its consitution (I *a*) was established by degradative studies by King *et al.*[1] but no synthetic support was provided. An obviously simple synthesis would be the C-methylation of the reactive methylene group of 2: 4-dihydroxy-4'-methoxy-desoxy benzoin. Badcock *et al.*[3] have shown that when heated with excess of methyl iodide and anhydrous potassium carbonate in acetone solution 2-hydroxy-4-methoxy- and 2-hydroxy-4 : 6-dimethoxy desoxy benzoins suffer α-methylation besides O-methylation. But when there was a methoxyl group in the benzyl part no C-methylation took place. This reaction has now been examined in detail using various modifications and has not been found to be suitable for the present synthesis.

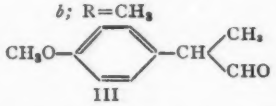


I

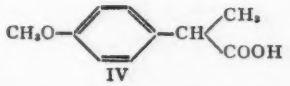
a; R=H
b; R=CH₃



II



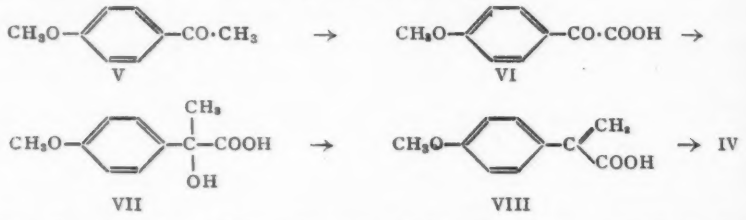
III



IV

Consequently an alternative method involving Friedel and Craft's reaction has been examined. *p*-Methoxy-hydratropic acid (IV) was needed for this purpose. This was originally prepared by Bougault[4] by the oxidation of anethole (II) first with iodine and mercuric oxide to *p*-methoxy-hydratropaldehyde (III) and then with silver oxide and alkali to *p*-methoxy hydratropic acid (IV). He reported that in many oxidations of the aldehyde to the acid the whole of the product got resinified. This has been our experience also. Hence the C-methylation of the ester and the nitrile of *p*-methoxy phenyl acetic acid was attempted with methyl iodide in the same way as with phenyl-acetonitrile and ethyl phenylacetate using sodamide[5] and also using sodium methoxide in methanol and anhydrous potssium carbonate in acetone

solution but the reactions were unsuccessful. This may be attributed to the adverse effect of the *p*-methoxyl group on the ionisation of the active methylene group. Finally the synthesis of *p*-methoxy-hydratropic acid (IV) has been conveniently carried out by the following route.



For the oxidation of *p*-methoxy-acetophenone (V) to *p*-methoxyphenyl glyoxalic acid (VI) with alkaline potassium permanganate a modification of the method of Bougault[6] has been employed giving a good yield. The second stage has been conveniently carried out by the Grignard reaction using methyl magnesium iodide in ether. *p*-Methoxy-atrolactinic acid (VII) was then dehydrated to *p*-methoxy-atropic acid (VIII) by following the procedure of Bougault[7] and final reduction to *p*-methoxy-hydratropic acid (IV) was accomplished using sodium amalgam and water.

The feasibility of Friedel and Craft's reaction using *p*-methoxy-hydratropic acid chloride was first tested using resorcinol dimethyl ether when angolensin-4-methyl ether (I *b*) was obtained satisfactorily and it agreed in its properties with the earlier description of King *et al.*[1] and with the sample prepared in this laboratory[2] from natural angolensin. Repetition of Friedel and Craft's reaction using O-dibenzyl resorcinol followed by debenzylation yielded angolensin (I *a*) identical with the racemic form of angolensin isolated from the wood of *Pterocarpus indicus*.[2]

EXPERIMENTAL

p-*Methoxy Phenyl Glyoxalic Acid* (*VI*)

This acid was first obtained by Bougault[6] by alkaline potassium permanganate oxidation of *p*-methoxy acetophenone in aqueous suspension at 0°. Owing to sparing solubility of the ketone the yield is poor. The following modified procedure gives a much better yield.

A solution of potassium permanganate (32 g.) and potassium hydroxide (12 g.) in water (600 c.c.) was added dropwise to a solution of *p*-methoxy acetophenone (12 g.) in pyridine (100 c.c.) at 15° with stirring during a period of four hours. The stirring was continued for one hour more and the unreacted permangante decomposed with sodium bisulphite. Manganese

dioxide that had separated was filtered off and washed with two 100 c.c. portions of water. The alkaline filtrate was acidified with concentrated hydrochloric acid (200 c.c.) and the solution left overnight in a refrigerator. Impure anisic acid (about 1 g.) that had separated out was filtered off, the filtrate saturated with sodium chloride, the solution extracted repeatedly with ether and the ether solution dried over magnesium sulphate. The residue after evaporation of ether crystallised from benzene-petroleum ether mixture as colourless thin and large rectangular plates, m.p. 87–88°. Yield, 6–7 g.

p-Methoxy-Atrolactinic Acid (*VII*)

This acid was obtained by Bougault[7] by permanganate oxidation of *p*-methoxy-hydratropic acid (IV). It has now been obtained from *p*-methoxy-phenyl glyoxalic acid (VI) by the Grignard reaction.

Magnesium powder (1·6 g., 3 mols) was added to a solution of methyl iodide (4·2 c.c.; 3 mols) in dry ether (100 c.c.) containing a trace of iodine. When the metal had completely dissolved, the ether solution was cooled to 0° and added dropwise to a solution of *p*-methoxy glyoxalic acid (4 g., 1 mol) in dry ether (100 c.c.) cooled in freezing mixture. After two hours standing in the freezing mixture a gummy solid was found to have separated out. The ether was decanted off and the solid treated with ice and dilute sulphuric acid when slowly it turned crystalline. It was extracted repeatedly with ether and the ether extract dried over magnesium sulphate. The residue after evaporation of ether crystallised from benzene as colourless prismatic needles and narrow rectangular plates, m.p. 129–30°.

p-Methoxy-Atropic Acid (*VIII*)

The following represents the best conditions for obtaining this acid by the method of Bougault.[8] A solution of *p*-methoxy-atrolactinic acid (5 g.) in glacial acetic acid (50 c.c.) was refluxed in an oil-bath at 130° for four hours. Acetic acid (about 40 c.c.) was distilled off under reduced pressure, the residue diluted with water (90 c.c.) and left at 0° for 24 hours when *p*-methoxy-atropic acid crystallised as colourless very thin plates, m.p. 118–20°. Yield, 2·5 g. A solution of the substance in glacial acetic acid decolorised bromine water.

p-Methoxy-Hydratropic Acid (*IV*)

Sodium amalgam (50 g., 2·5%) was added with constant shaking to a solution of *p*-methoxy-atropic acid (1 g.) in 2% aqueous sodium hydroxide (50 c.c.) and was left overnight. The brown alkaline solution was separated from mercury and acidified with concentrated hydrochloric acid when a semi-solid mass separated out which was repeatedly extracted with ether and the ether solution dried over magnesium sulphate. After the distillation of ether

the residue crystallised from benzene-petroleum ether mixture as colourless irregularly-shaped plates, m.p. 55–57°. Yield, 0·8 g. It did not decolorise bromine water in glacial acetic acid solution.

Angolensin-4-methyl Ether (*I b*)

The chloride of *p*-methoxy hydratropic acid (IV) was prepared as follows: To a solution of the acid (2 g.) in dry chloroform (25 c.c.) was added phosphorus trichloride (0·6 g., 1/3 mol.) dropwise with shaking and cooling. The reaction mixture was left at room temperature for two hours with occasional shaking, heated to 60° for two minutes and the chloroform solution separated from the phosphorous acid that had separated. On distilling off chloroform under reduced pressure the acid chloride was left behind as a very pale yellow viscous oil which was directly used for the Friedel and Craft's reaction.

A solution of anhydrous aluminium chloride (8 g.) was prepared in dry ether (80 c.c.) with cooling in ice. To this was added resorcinol dimethyl ether (1·6 g.) and then an ether solution of the acid chloride prepared as above. The mixture was left at room temperature overnight. The next day as much of ether as possible was distilled off, the complex decomposed with ice and hydrochloric acid and extracted with ether. The ether solution was separated into aqueous sodium bicarbonate soluble fraction (A), sodium carbonate soluble fraction (B), sodium hydroxide soluble fraction (C) and the neutral fraction (D). Fraction (A) gave a small amount of unchanged acid; fraction (B) gave none on acidification and fraction (D) yielded a small amount of resorcinol dimethyl ether and hence all these were rejected. Fraction (C) on acidification gave a viscous oil which was extracted with ether and the ether solution dried over sodium sulphate. The residue left after removal of ether was distilled under reduced pressure when angolensin-4-methyl ether passed over at 230–33° at 2·3 mm. pressure. It gave a reddish brown colour with alcoholic ferric chloride and a green colour with concentrated nitric acid. Yield, 1·2 g. King *et al.*[1] recorded 240–50° as bath temperature at 0·3 mm. pressure.

The filter-paper chromatography of synthetic angolensin-4-methyl ether and the one prepared from natural angolensin by the procedure of Gupta and Seshadri[2] gave the same brown ring, R_F, 0·83 at 36° using 15% isopropyl alcohol as the solvent and diazotised benzidine reagent as the developer. The oxidation of synthetic angolensin-4-methyl ether with potassium permanganate in acetone solution was carried out by the procedure of Gupta and Seshadri[2] whereby *p*-methoxy-acetophenone, anisic acid and *p*-methoxy salicylic acid were isolated.

Angolensin (*I a*)

Using the same procedure and resorcinol dibenzyl ether (3·2 g.) and the acid chloride from *p*-methoxy-hydratropic acid (2 g.) crude angolensin-4-benzyl ether was obtained. Yield, 0·5 g. Small amounts of unchanged acid and resorcinol dibenzyl ether were recovered but the poor yield should be ascribed to the resinification that takes place during the reaction.

The benzyl ether (0·5 g.) was dissolved in glacial acetic acid (20 c.c.) and concentrated hydrochloric acid (20 c.c.) added. The mixture was heated on a boiling water-bath for one hour, poured over ice and extracted repeatedly with ether. The ether extract was washed with aqueous sodium bicarbonate to remove acetic acid and then extracted with 5% aqueous sodium carbonate. The carbonate solution was acidified, extracted with ether and the ether solution dried over sodium sulphate. The residue after removal of ether crystallised from benzene-petroleum ether mixture as small prisms and plates, m.p. 118–20° alone or admixed with an authentic sample of racemic angolensin isolated from *Pterocarpus indicus*.[2] It gave a reddish brown colour with alcoholic ferric chloride, R_F, 0·72 (brown ring) at 36° using the organic layer of methanol-chloroform-ligroin-water (1 : 2 : 7 : 5) mixture as the solvent and diazotised benzidine reagent as the developer was obtained with both synthetic and natural samples and with a mixture of the two.

Summary

By the Friedel and Craft's reaction using resorcinol dimethyl ether and *p*-methoxy hydratropic acid chloride, angolensin monomethyl ether has been prepared. Employing resorcinol dibenzyl ether for the reaction and final debenzylation, angolensin (racemic) itself has been obtained.

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STUDIES OF GALLIC ACID COMPLEXES WITH METALS AND THEIR ANALYTICAL APPLICATIONS

Part II. A Spectrophotometric Study of Molybdenum Complexes

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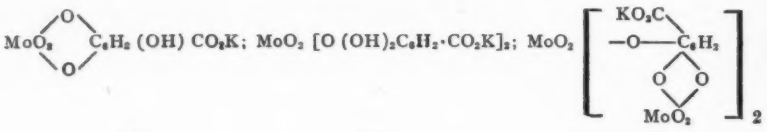
(Communicated by Dr. H. J. Bhabha, F.R.S., F.A.SC.)

Introduction

Fernandes[1] has reported the preparation of numerous compounds of various hydroxy organic acids with molybdic and tungstic acids and has mentioned three distinct complexes of molybdic oxide with potassium gallate in the ratio 1, 2 and 0·66 moles of gallate per mole of MoO_3 to which the following formulæ have been assigned respectively:—



(i) (ii) (iii)

These were obtained by treating solutions of potassium gallate with calculated quantities of the molybdenum oxide and concentrating the solutions when the compounds crystallised out. However in a subsequent communication[2] on the complexes of other hydroxyacids with MoO_3, WO_3 and UO_3 it has also been stated that in aqueous solutions compounds of the first type, *viz.*, 1 : 1 complexes, are normally obtained but a very large excess of the phenol is required to give complexes of the second type.

Pozzi-Escot[3] has utilised the yellow to orange colour given by molybdates in presence of polyphenols, such as gallic and pyrogallic acids, for the detection of molybdenum.

The work presented in this paper was undertaken firstly to find out by spectrophotometric method, under controlled conditions of pH, etc., the evidence for the formation of the various compounds reported and secondly to find out the feasibility of utilising the colour formation for the quantitative estimation of molybdenum.

Experimental

Apparatus and Reagents

Instruments.—pH measurements were made on a Marconi pH meter, type TF 511 D. Spectrophotometric measurements were done on a Beckman Model DU Quartz Spectrophotometer using 1 cm. quartz absorption cells.

Gallic acid.—E. Merck, G. R. recrystallised and dried at 120° C. Fresh solutions were prepared when required.

Sodium molybdate.—B.D.H. Analar molybdic acid dissolved in a little more than the stoichiometric quantity of sodium hydroxide solution (from E. Merck, G.R. grade) and standardised by gravimetric estimation as lead molybdate.

Sodium acetate.—E. Merck, G.R. grade.

Sulphuric acid.—E. Merck, G.R. grade.

Absorption Spectra

The absorption spectra of the two reactants, *viz.*, sodium molybdate in $2{\cdot}8 \times 10^{-5}$ M concentration, gallic acid in $1{\cdot}5 \times 10^{-4}$ M concentration and of the complex formed by mixing these, all at a pH of 4·2, are presented in Fig. 1. The optical density values for the complex have been obtained after allowing for the absorption due to the two reactants. The curve shows a single absorption peak at 305 mμ.

Absorption measurements were also carried out with more concentrated solutions in the region of 300–600 mμ using ratios of molybdic acid: gallic acid as 1:1, 1:4 and 1:10·5. No characteristic absorption was observed in any case as seen from Fig. 2 (plotted up to 500 mμ only).

Effect of pH

Preliminary experiments had shown that the formation of the molybdenum-gallic acid colour was extremely sensitive to hydrogen-ion concentration and showed maximum absorption in the pH range of 4–4·5 beyond which a sharp decrease in the absorption was noticed. The results obtained at 320 mμ are shown in Fig. 3. As the absorption of gallic acid is affected by the change in pH,[4, 5] this effect was obviated by taking gallic acid solutions of corresponding pH as blanks.

The same effect was observed in the absorption spectra in the region of 250–375 mμ by taking molybdic acid and gallic acid in the ratio of 1:4 and changing the pH (Fig. 4).

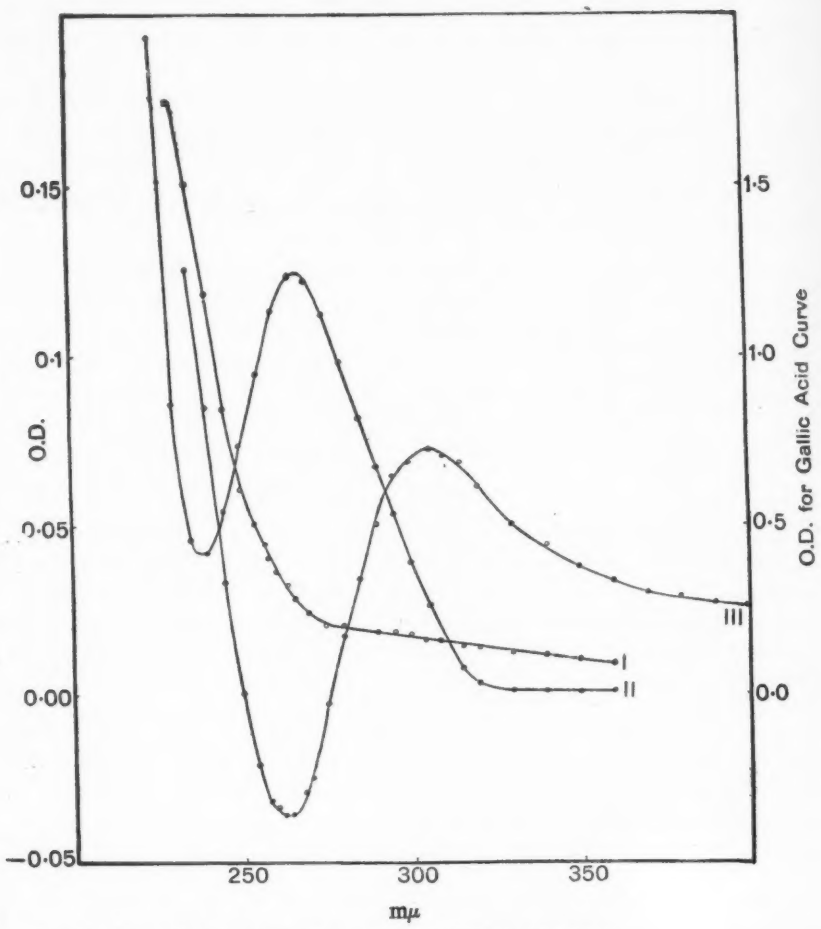


FIG. 1. Absorption Spectra:—Curve I: $2{\cdot}8\times10^{-5}$ M. Molybdate.
,, II: $1{\cdot}5\times10^{-4}$ M. Gallic Acid.
,, III: Complex, $2{\cdot}8\times10^{-5}$ M. in Molybdate and $1{\cdot}5\times10^{-4}$ M. in Gallic Acid (all at pH 4·2)

In all further experiments therefore the pH was adjusted to 4·2.

COMPOSITION OF THE COMPLEX

The ratio of Mo to gallic acid in the complex or complexes was investigated by three different methods, *viz.*, (*a*) method of continuous variations,[6,7] (*b*) the molar ratio method[8] and (*c*) the modified slope ratio method.[9,10]

Since molybdenum is stated to form more than one complex with gallic acid it was necessary to find out suitable wavelengths at which measurements for the various complexes could be made.

Absorption spectra of the solutions were first obtained where molar ratios of Mo to gallic acid were varied. These absorption curves above the wavelength of 300 mμ are shown in Fig. 2. Owing to high absorption of

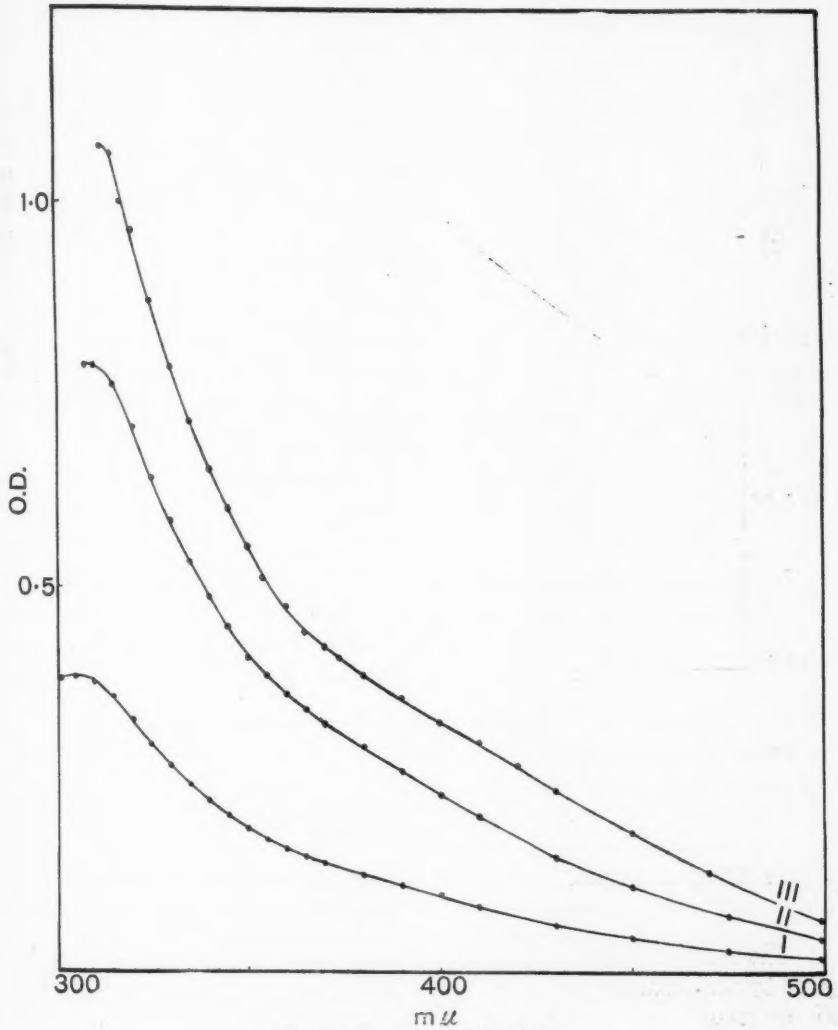


FIG. 2. Curve I: Ratio 1:1
" II: " 1:4
" III: " 1:10·5

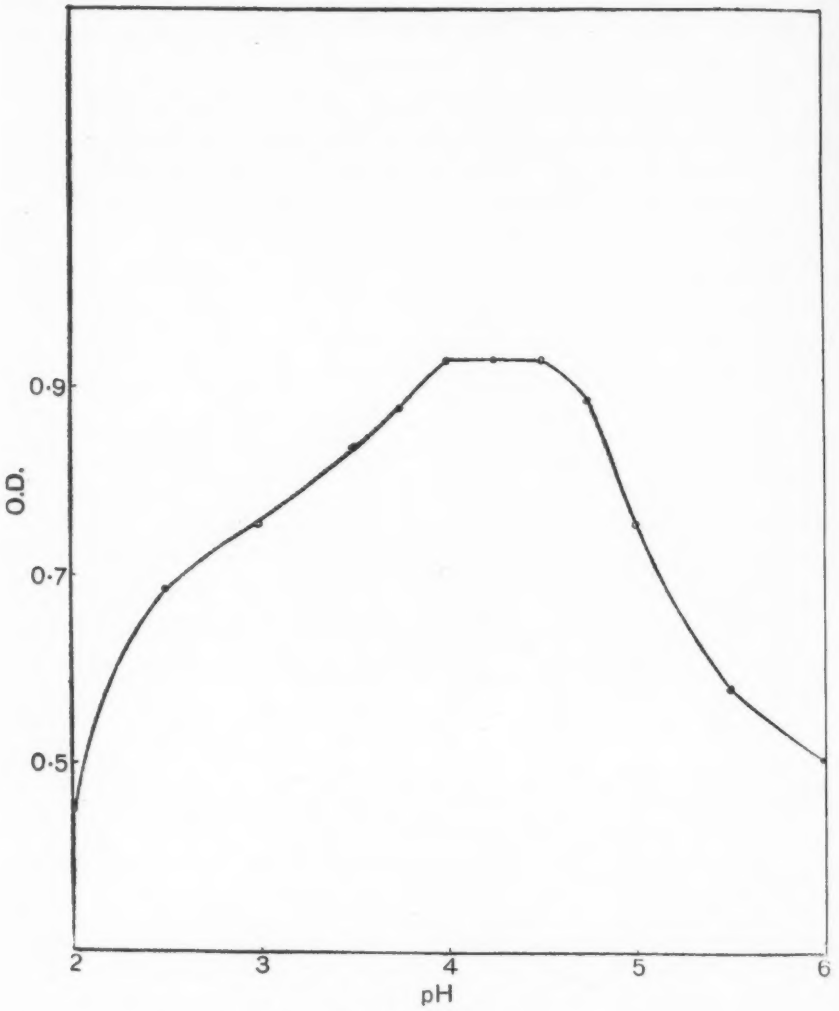


FIG. 3. Effect of pH.

gallic acid in the ultraviolet region it was not possible to make measurements in the region lower than 300 mμ for solutions containing high ratio of gallic acid to molybdenum. Similarly curves II and IV of Fig. 4 show the absorption spectra of solutions containing molybdenum: gallic acid in the ratios of 1:4 and 1:1 respectively all the other conditions being constant.

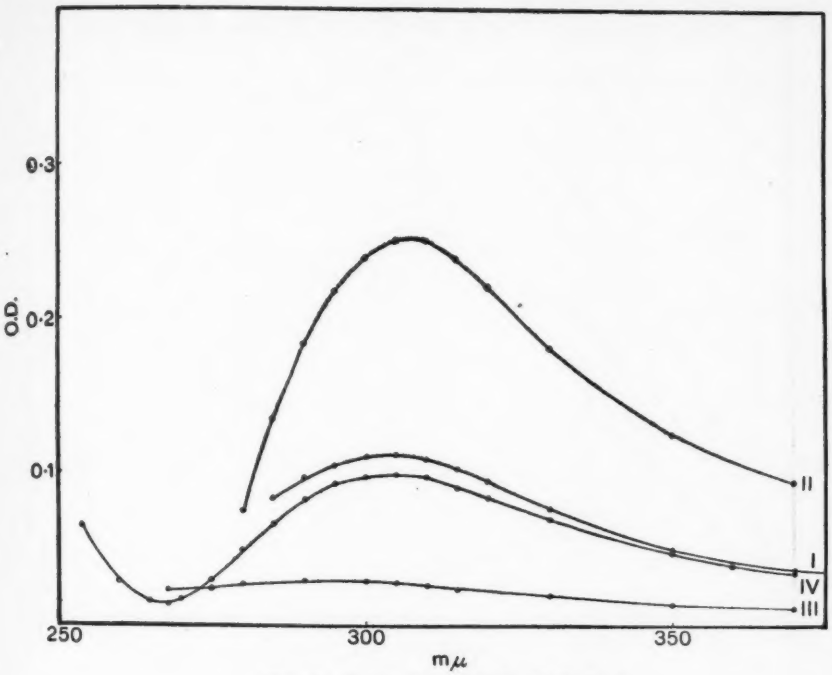


FIG. 4. Curve I: pH 2·5; Ratio 1:4.
„ II: „ 4·2; „ 1:4.
„ III: „ 6·0; „ 1:4.
„ IV: „ 4·2; „ 1:1.

The spectral data does not in the least indicate the formation of more than one complex in the solutions or alternately if more complexes do exist they have similar absorption characteristics.

(*a*) *Method of Continuous Variations*

In the absence of any characteristic wavelengths of absorption for different complexes, if at all they are present, the study of the system by the method of continuous variation was made at three wavelengths, *viz.*, 300 and 315 mμ which are near the maximum absorption wavelength of the complex and at 360 mμ where the reactants themselves will have a very low absorption.

A series of solutions was prepared in which the ratios of molybdenum to gallic acid was varied but the total molarity of the two was constant, the pH also being kept constant at 4·2, and their optical densities were measured. Fig. 5 shows the results obtained at wavelengths of 300, 315 and 360 mμ

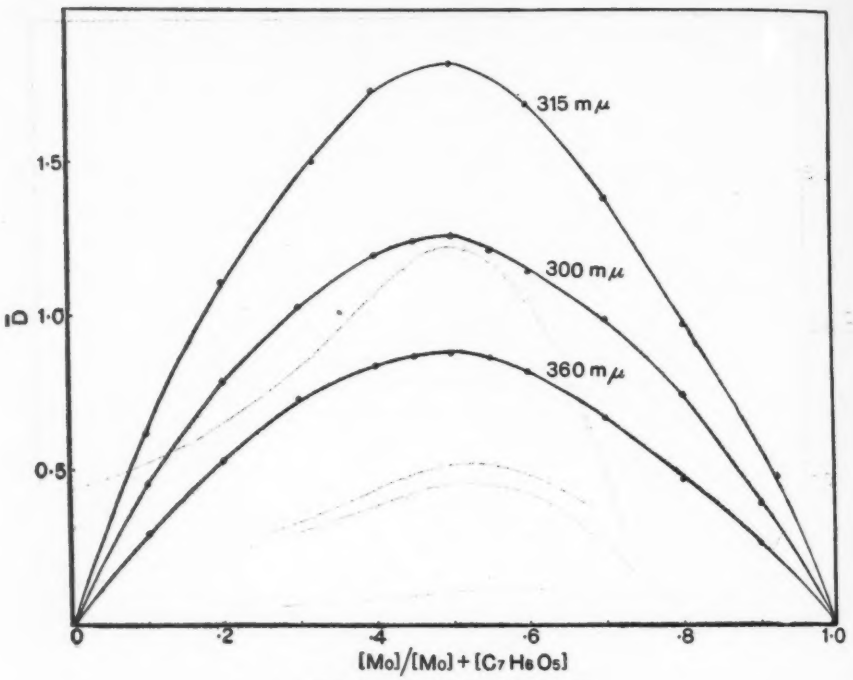


FIG. 5. Continuous Variations.

where the difference (D) between the observed optical density of each solution and that calculated on the assumption that there is no reaction between the two reagents have been plotted against the ratio [Mo]/[Mo] + [$C_7H_6O_5$]. For convenience of representation the values of $\overline{D}$ for the wavelength of 300 mμ have been multiplied by a constant factor in Fig. 5.

In all the three curves the maximum absorption occurs when the relative proportion of gallic acid to molybdenum is 1 : 1 forming a complex which from the nature of the graphs indicates that it is highly dissociating in solution.

(*b*) *Molar Ratio Method*

Fig. 6 shows the effect of increasing the molar concentration of one of the reagents at a fixed concentration of the other, the measurements being made at 380 mμ. Owing to the high dissociation of the complex the curves do not show any sharp break. Attempts were made to get a sharp break in the curve by increasing the ionic concentration of the solutions by addition

of potassium chloride. A slight increase in the optical densities was observed but the increase was so slight as not to be of any consequence.

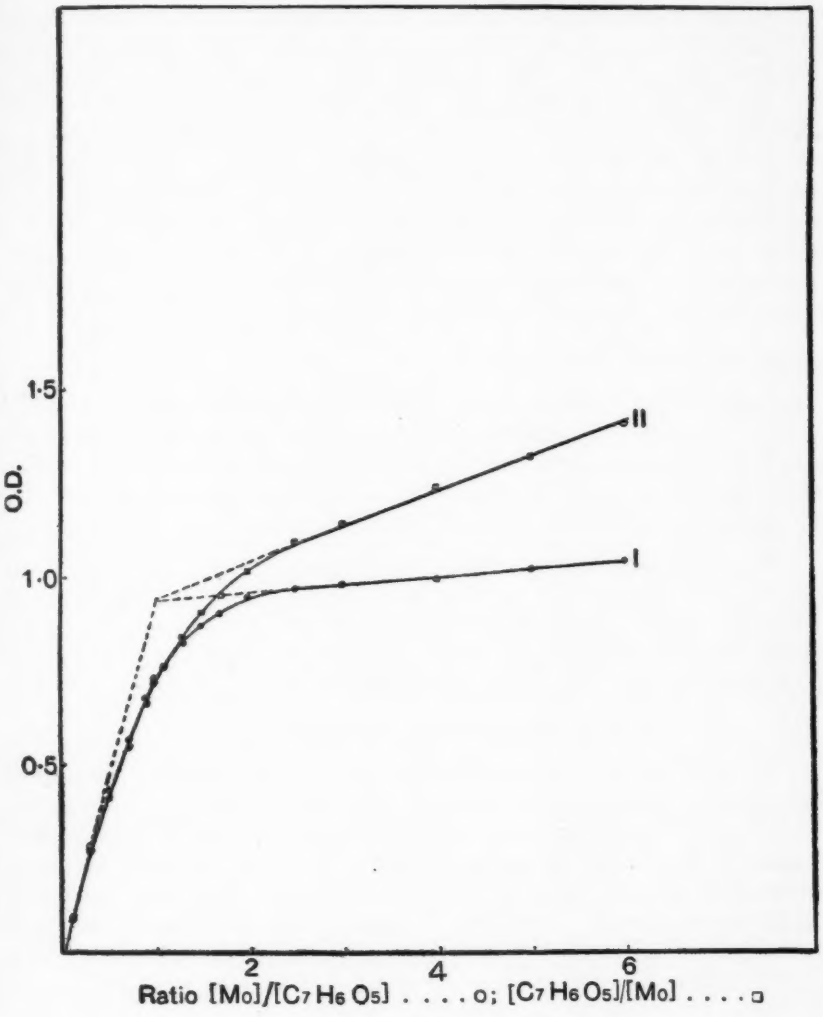


FIG. 6. Molar Ratio.

The dotted lines in the figure are expected to present the true curves on the assumption that there was no dissociation of the complex in which case

the point of intersection corresponds to a molar ratio of molybdenum: gallic acid as 1:1.

Further it may be noted that curve I (Fig. 6) in which the concentration of molybdenum is varied with respect to a constant concentration of gallic acid levels off to a reasonably constant optical density, whereas in curve II the optical density was still found to be rising even at a molybdenum: gallic acid ratio of 1:6. In fact increasing the ratio of molybdenum: gallic acid up to 1:50 still showed increasing values in optical density. This may possibly be due to the formation of only 1:1 complex in the former case while in the latter case the second complex of molybdenum (Mo: gallic acid:: 1:2 as previously reported) is probably formed as more and more gallic acid is made available. No direct evidence for the formation of the molybdenum: gallic acid:: 1:2 complex was however obtained.

(*c*) *Modified Slope Ratio Method*

Raghava Rao and co-workers[9, 10] have used a modified slope ratio method in which they plot the optical densities *versus* the concentration of the variable components from either end of the X-axis, thus giving two plots which intersect at a point corresponding to the composition of the complex, the assumption being that only one complex is formed.

In the discussion under "Molar ratio method" it has been shown that a large excess of gallic acid increases the optical density of the solutions continuously. Restricting therefore to molar ratio of one reactant up to 2 with respect to 1 mole of the other a plot is obtained as given in Fig. 7, which once again gives the ratio of molybdenum: gallic acid in the complex as 1:1.

DISSOCIATION CONSTANT

The dissociation constant of the complex was calculated by the method described by Anderson and co-workers.[11, 12] Assuming that the extreme end of curve I of Fig. 6 represents complete colour saturation for the quantity of gallic acid used (0·0005 gramme moles in one litre), the molar extinction coefficient of the complex was calculated. From the absorbancy values and the known concentrations of the two reactants, the equilibrium concentrations of the complex and the two reactants were calculated. From these the dissociation constant (K) was calculated. The average value for

$$K = \frac{[Mo]\,[R]}{[MoR]} = 0{\cdot}6 \times 10^{-4} \pm 0{\cdot}1 \times 10^{-4}$$

where R represents gallic acid.

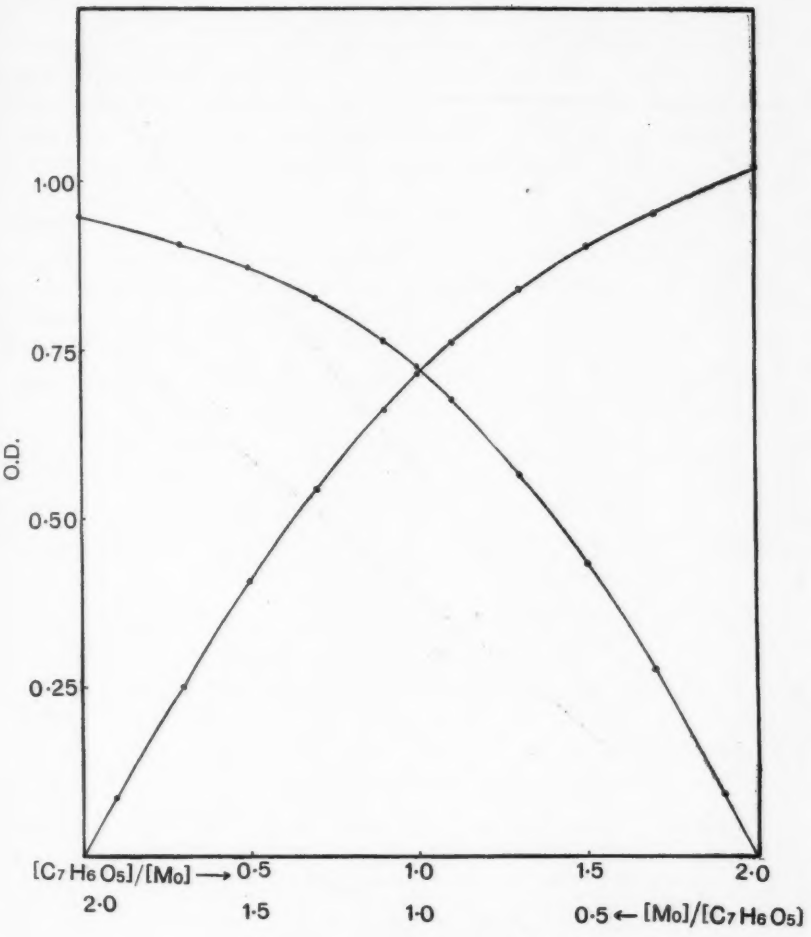


FIG. 7. Modified Slope Ratio.

ESTIMATION OF MOLYBDENUM

Contrary to the observations of Pozzi-Escot[3] it was found that by maintaining pH constant at 4·2 Beer's law was valid for the ranges studied, *viz.*, 0·01 to 0·10 mg. and 0·10 to 1 mg. of molybdenum per 100 c.c. of solution in the presence of 15 mg. and 150 mg. respectively of gallic acid. Measurements were preferably taken at wavelengths of 330 mμ and above as

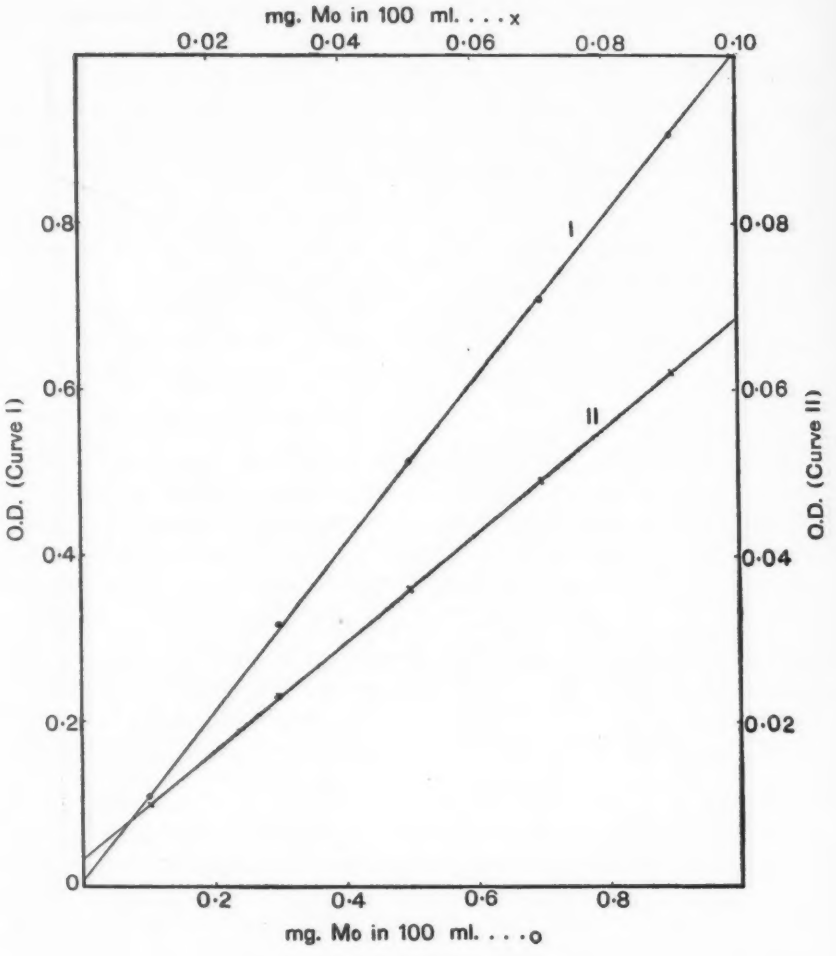


FIG. 8. Beer's Law Curves (330 mμ).

the absorbancy due to gallic acid is low in this region. The colours are developed immediately and were found to be stable up to 24 hours.

The graphs as given in Fig. 8 for the two ranges of molybdenum concentration studied show different slopes. It may be remembered however that the excess of gallic acid used in the two sets is very much different.

Interferences

A number of metal ions such as Fe, Ti, V, W, etc., interfered in the estimation. This interference could not be easily removed. Addition of complexing agents like tartaric and oxalic acid or E.D.T.A. either diminished the molybdenum colour or destroyed it completely. It is therefore necessary to isolate the molyebdnum before developing the colour.

Sensitivity

Rice and Yerkes[13] have reported the sensitivities of various reagents used for molybdenum estimation. A comparison of these with the present method is given below:—

Reagent	Sensitivity in g. of Mo per litre
Potassium ferrocyanide	0·1
Sodium thiosulphate	0·04
Phenyl hydrazine	0·006
Potassium xanthate	0·004
Butyl xanthate	0·004
Amyl xanthate	0·004
Pentasol xanthate	0·004
Potassium ethyl xanthate (colour extracted with ether)	0·0004
Gallic acid	0·0001 (O.D. = 0·01)
Ammonium thiocyanate-stannous chloride (colour extracted with ether)	0·00002

Summary

Spectrophotometric study of the molybdenum-gallic acid system showed the formation of a yellow complex of the empirical formula MoR which shows an absorption maximum at 305 mμ. The complex dissociates appreciably in solution and gave the value for K, the dissociation constant as $0{\cdot}6 \times 10^{-4} \pm 0{\cdot}1 \times 10^{-4}$. Beer's law was found to hold good for concentrations up to 1 mg. Mo per 100 c.c. and quantitative estimations could be made after isolation of Mo from interfering elements.

The authors are thankful to Mr. M. S. Das, Mr. Ch. Venkateswarlu and Mr. G. K. Belekar for valuable suggestions.

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STUDIES OF GALLIC ACID COMPLEXES WITH METALS AND THEIR ANALYTICAL APPLICATIONS

Part III. Spectrophotometric Estimation of Gallic Acid

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Introduction

The reaction between gallic acid and ferrous sulphate in tartrate medium has been employed for the colorimetric estimation of gallic acid.[1, 2, 3] Glasstone[4] has reported the use of osmium tetroxide as a colorimetric reagent. Mattil and Filer[3] have developed a spectrophotometric method based on the ultraviolet absorption of gallic acid itself at 270–71 mμ in 0·01 N hydrochloric acid.

In connection with some work on the metal-gallic acid complexes in this laboratory (yet to be communicated), a rapid colorimetric method for estimating gallic acid was required. For this purpose, none of the above-mentioned methods were found to be very well suited chiefly because of the very low concentration of gallic acid (1·6 mg. gallic acid/100 ml.—maximum) estimated.

It was felt that the titanium-gallic acid system[5] could be utilised for the estimation of gallic acid, provided the hydrolysis of the excess titanium salt, required for colour saturation, could be prevented by the addition of another complexing agent, which would not otherwise interfere with the formation of the coloured complex. To this end, the effect of tartrate, oxalate and citrate ions on this system has been studied and the results are described in this paper.

Apparatus and Reagents

Same as in Part I (*loc. cit.*)

Ammonium oxalate
Ammonium tartrate
Ammonium citrate
} B.D.H., AnalaR

Experimental

Preliminary experiments are carried out using ammonium tartrate as the complexing agent for the excess titanium. The relative proportion of ammonium tartrate to titania is arbitrarily fixed as 10: 1 (w/w) in the begin-

ning. The pH of the final solutions is always about 5·0. Under these conditions, the following observations are made:

(i) The coloured complex shows maximum absorption at 370 mμ in the region 300–500 mμ.

(ii) The colorimetric titration at 370 mμ with 2·0 mg. of gallic acid in a total volume of 100 ml. reveals that, though the colour saturation is more or less complete when 2·5 mg. of titania and 25 mg. of ammonium tartrate are added, it is not quantitative even after the addition of 10 mg. of titania and 100 mg. of the tartrate.

(iii) The calibration curves, studied between 370 and 450 mμ are linear showing that Beer's Law is obeyed but they show a varying positive Y intercept and,

(iv) the extinction values for the same amount of gallic acid are varying with variation of the quantity of titania used as well as with the relative proportion of the tartrate to titania.

In view of the above observations, the role of tartrate in the system is further investigated as follows:—

1·0 mg. of titania and 0·25 mg. gallic acid (mole ratio: approximately 8: 1) are taken in different flasks. Varying amounts of the tartrate are added, pH adjusted to about 5·0 with 2 N ammonium acetate, and the volumes made up to 50 ml. Extinctions are measured at 370 mμ and plotted against the concentration of the tartrate (Fig. 1 *a*). It will be seen that the extinction first goes down, then rises to a more or less steady value and drops again slowly with further addition of tartrate. It is evident from this, that colour development is maximum when the tartrate concentration is 20 to 28 mg. (approximately corresponds to 9–12 moles of the tartrate for a mole of titania). The same experiment is repeated with different amounts of titania and the same amount of gallic acid, and in every case, the maximum colour formation is obtained when the ratio of the tartrate to titania is the same as found before.

Similar experiments using ammonium oxalate and citrate (Figs. 1 *b* and 1 *c*) show that these two complexing agents do prevent the hydrolysis of the titania but interfere seriously with the formation of the coloured complex.

In all further experiments, a ratio of 1: 25 (w/w) between titania and ammonium tartrate is maintained and this mixture is hereafter referred to as ' titanium tartrate,' the concentration of the mixture being expressed in terms of the titania content.

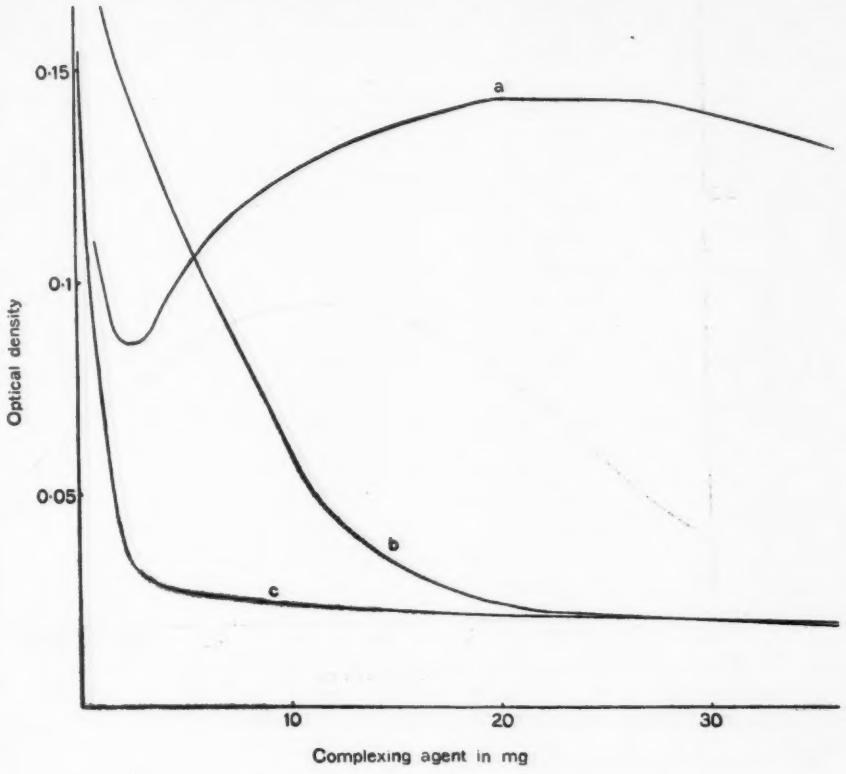

FIG. 1

a—Role of Tartrate;
b—Role of Oxalate;
c—Role of Citrate;
Gallic acid—0·25 mg. } in 50 ml.
Titania—1·0 mg. }

Absorption Spectrum of the Complex

0·5 mg. of gallic acid is complexed with excess 'titanium tartrate' in a total volume of 50 ml. and the absorption spectrum has been studied against reagent blank between 300 and 500 mμ. It shows maximum absorption at 370 mμ (Fig. 2).

Effect of pH

The effect of hydrogen-ion concentration is studied in the presence of tartrate. Maximum colour development is attained at pH 4·0–7·0 (same as in the case of $TiGa_6$[5]).

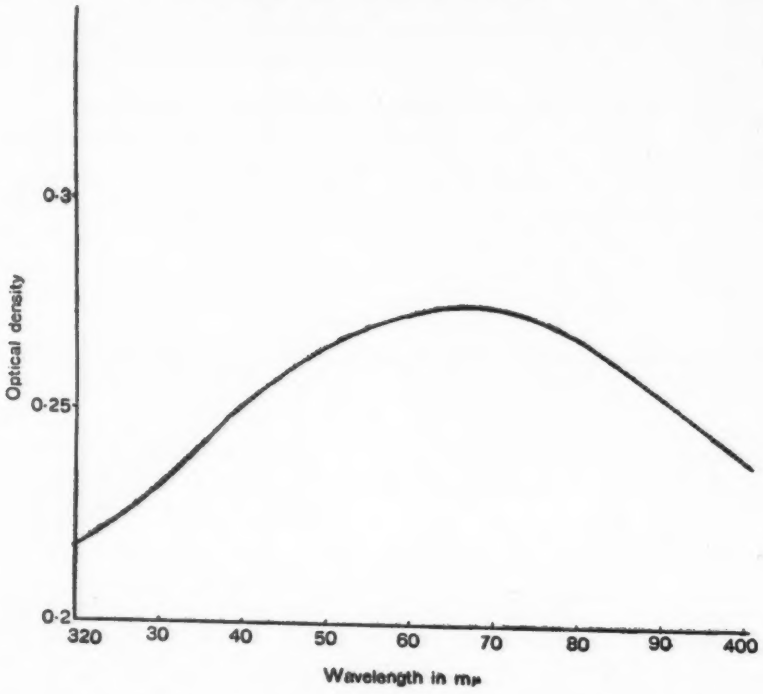

FIG. 2. Absorption spectrum of the complex with 0·25 mg. gallic acid in 50 ml.

Effect of Reagent Concentration

The colorimetric titration is carried out with 1·0 mg. gallic acid in 50 ml. following the same procedure given in Part I (*loc. cit.*). It is evident from Fig. 3 that colour development reaches the saturation limit this time, whereas preliminary experiments with a different amount of the tartrate have shown a continuous increase with increase of the reagent.

Estimation of Gallic Acid

Varying amounts of gallic acid are taken, 'titanium tartrate' is added in excess (2·5 to 5·0 mg. of TiO_2 per 1·0 mg. of gallic acid), pH is adjusted as before with 2 N ammonium acetate to about 5·0 and the volumes are made up to 50 ml. The optical densities are measured at 370 mμ or at higher wavelength depending on the concentration of gallic acid taken, and plotted against the concentration of gallic acid. The slopes for a concentration range of 0·1 to 2·0 mg. of gallic acid in 50 ml. at 370, 400 and 450 mμ are shown in Fig. 4. Now the calibration curves are not only linear but also pass through

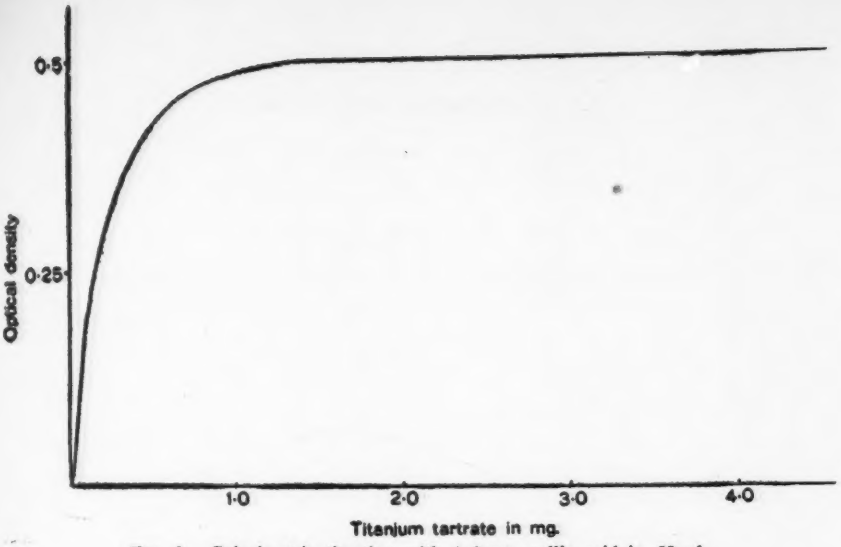

FIG. 3. Colorimetric titration with 1·0 mg. gallic acid in 50 ml.

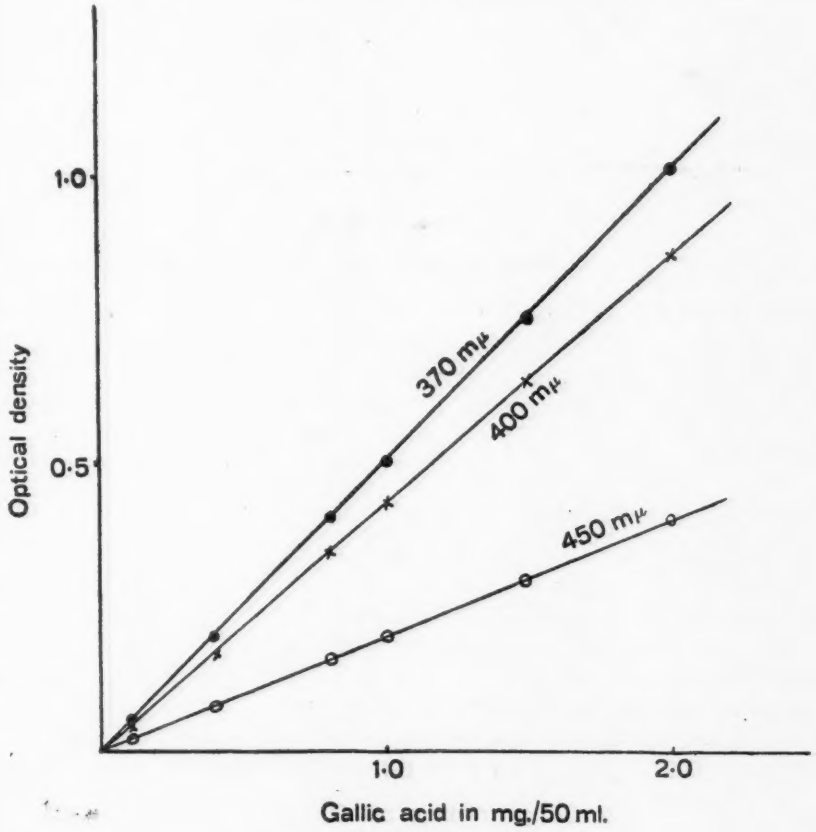

FIG. 4. Calibration curves.

the origin. Using the above procedure, the maximum amount of gallic acid estimated is 10 mg. in a total volume of 50 ml. The method, thus, is accurate and very rapid over a wide range of gallic acid concentration.

For the calibration purposes, only ' M and B ' titania is used.

A study of the entire titanium-gallic acid system in the presence of these complexing agents is under further investigation.

SUMMARY

A comparative study of the influence of tartrate, oxalate and citrate ions on the titanium-gallic acid system, when titania is in excess, shows that the oxalate and citrate ions interfere seriously in the formation of the coloured complex. In the case of tartrate, maximum colour development is attained when the amount of ammonium tartrate is 20 to 28 times (w/w) to that of titania. Based on this, a spectrophotometric method has been described for the estimation of gallic acid over a wide concentration range.

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